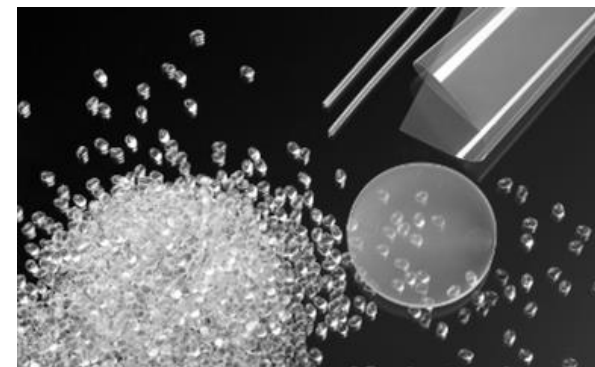


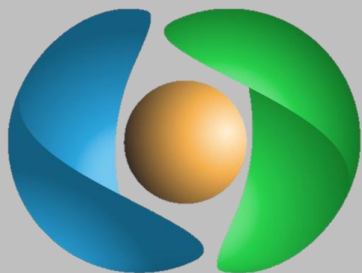
# Conference Guide



Working Party on  
**Polymer Reaction Engineering**

9<sup>th</sup> PhD-Workshop on Polymer Reaction Engineering  
23<sup>rd</sup> November to 25<sup>th</sup> November 2021 (online event)





# Welcome to the 9<sup>th</sup> PhD-Student Workshop on Polymer Reaction Engineering

Dear PhD-students, professors and company representatives,

the PhD-Student Workshop on Polymer Reaction Engineering represents an international platform where young researchers in the field of polymer reaction engineering have the opportunity to get into contact with fellow PhD-students but also to meet various industry representatives and potential employers personally. Moreover, PhD-students can benefit from useful feedback on their work and improve their soft skills by practicing the presentation of complex scientific topics.

The workshop is being held for the ninth time now. It has been launched in Lyon in 2012 with a total number of 35 participants. In 2019, we recorded a number of 49 registrations in Hamburg. Due to the pandemic, no workshop was held in 2020. For 2021, we decided to temporarily switch to an online format in order to provide PhD students with an opportunity to present their work. The next workshop is already in planning and will be held face-to-face in San Sebastian Spain from April 20<sup>th</sup> to 22<sup>nd</sup> 2022.

As always, this year's topic are excitingly diverse:

- process advancements as well as new methods of inline-spectroscopy
- synthesis of homopolymers, copolymers, blends and hybridpolymers
- bulk-, emulsion-, catalytic- and high-pressure polymerization
- modeling of chemical reaction networks: deterministic and stochastic
- focusing on structure-property relationships and thermodynamics

With all these topics ahead, we are looking forward to an informative workshop!

## Organizing Committee

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Prof. Dr. Markus Busch	Chair of WPPRE, TU Darmstadt
Dr. Kristina Zentel	Secretary of WPPRE, TU Darmstadt
Laura Euler Bueno	TU Darmstadt
Elisabeth Nowotny	TU Darmstadt

## Sponsors

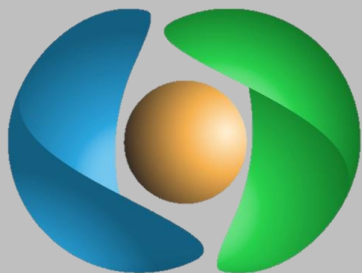
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Due to the temporary switch to an online format, no „classic“ sponsoring of social events takes place this year.

Nevertheless, we are happy to welcome industry representatives from Wiley-VCH, Hungenberg Consultant, Evonik, DSM, Sabic, BASF, Wacker, Sulzer and Arlanxeo to this year's workshop.

Despite the special circumstances, we are delighted and want to warmly thank Wiley-VCH for sponsoring a best contribution prize for the online event!

**WILEY**



# Program by Days

## Tuesday, 23<sup>rd</sup> November 2021

13:00 - 13:10 **Prof. Dr. M. Busch, Dr. Kristina Zentel**  
*Welcome*

13:10 - 13:15 **Elisabeth Nowotny** (TU Darmstadt)  
*Technical notes on presentation session*

~~~~~ **Session I: Inline Spectroscopy** ~~~~~

*Chair: Elisabeth Nowotny (TU Darmstadt)*

13:15 - 13:35 **Stephanie Schlappa** (University of Potsdam)  
*Inline monitoring of nanosized polymer materials using  
Photon Density Wave spectroscopy*

13:35 - 13:55 **Laurence Jacob** (University of Hamburg)  
*Inline monitoring of latex-particle size distribution in  
emulsion polymerisation process*

13:55 - 14:10 **Elisabeth Nowotny** (TU Darmstadt)  
*Technical notes on breaks and poster sessions*

14:10 - 14:30 **Break**

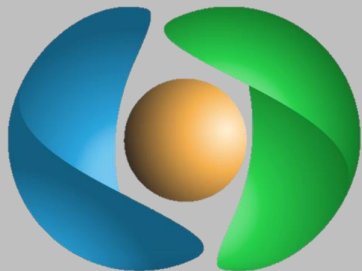
14:30 - 15:15 **Poster session**

15:15 - 15:35 **Break**

15:35 - 16:05 **Introduction of industry representatives**

16:05 - 17:05 **Social event**

17:05 - 17:10 **Elisabeth Nowotny**  
*Farewell*



# Program by Days

## Wednesday, 24<sup>th</sup> November 2021

13:00 - 13:05 **Laura Euler Bueno**  
*Welcome*

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### *Session II: Waterborne Coatings*

*Chair: Isabel Kronshorst (TU Darmstadt)*

13:05 - 13:25 **Sumi Murali Nair** (University of the Basque Country)  
*Use of zwitterionic monomers for colloidal stabilization of waterborne polymer dispersions*

13:25 - 13:45 **Elvis Lopes Brito** (University of the Basque Country)  
*Film Formation of Core-Shell Latex Particles*

13:45 - 14:05 **Sheraz Tariq** (University of the Basque Country)  
*Study of the inter-particle crosslinking reactions in waterborne coatings*

14:05 - 14:25 **Hesham Abdeldaim** (University of the Basque Country)  
*Soft Core-Hard Shell Latex Particles for Cracking Free Thick Polymer Coatings*

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14:25 - 14:45 **Break**

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14:45 - 15:30 **Poster session**

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15:30 - 15:50 **Break**

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### *Session III: Modelling*

*Chair: Jonas Degenkolb (TU Darmstadt)*

15:50 - 16:10 **Stefan Welzel** (University of Stuttgart)  
*Fouling in continuously operated tubular reactor for the radical polymerization of N-Vinylpyrrolidone*

16:10 - 16:30 **Andreas Feuerpfeil** (TU-Clausthal)  
*Monte Carlo simulation of non-isothermal semi-batch vinyl acetate polymerization under industrial important conditions*

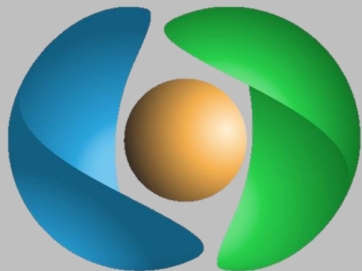
16:30 - 16:50 **Elisabeth Nowotny** (TU Darmstadt)  
*Development of a Model for the Free-Radical Copolymerization of Ethylene and Vinyl acetate*

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16:50 - 16:55 **Dr. Kristina Zentel**  
*Farewell*

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16:55 - 18:30 **optional get-together on [wonder.me](https://wonder.me)**



# Program by Days

## Thursday, 25<sup>th</sup> November 2021

13:00 - 13:05 **Elisabeth Nowotny**  
*Welcome*

### ~~~~~ *Session IV: Processes* ~~~~~

*Chair: Lena Gockel (TU Darmstadt)*

13:05 - 13:25 **Daniela Eixenberger** (Hamburg University of Technology)  
*Smart Reactors - Surface Enhancement of Additively  
Manufactured Structures by ARGET ATRP*

13:25 - 13:45 **Jana Sklenářová** (UCT Prague)  
*How to increase the Selectivity of the Triboelectric  
Separation of Plastic Waste?*

13:45 - 14:05 **Wasif Razzaq** (University of Strasbourg)  
*Microfluidic-Assisted Synthesis of Polymeric Microfibers*

14:05 - 14:25 **Vida Gabriel** (University of Ottawa)  
*Incorporating Carboxylated Cellulose Nanocrystals in  
Latexes for Adhesive Applications: A Sticky Situation*

14:25 - 14:45 **Break**

14:45 - 15:15 **Poster session**

15:15 - 15:35 **Break**

### ~~~~~ *Session V: solution polymerization & thermodynamics* ~~~~~

*Chair: Jana Sartorius (TU Darmstadt)*

15:35 - 15:55 **Isabel Kronshorst** (TU Darmstadt)  
*Method for the Determination of Reactivity Ratios  
at High Conversions in the Continuous Solution  
Polymerisation Process*

15:55 - 16:15 **Jakub Klimošek** (UCT Prague)  
*Experimental and Theoretical Study of Small  
Hydrocarbons Diffusion in Semi-Crystalline Polyolefins*

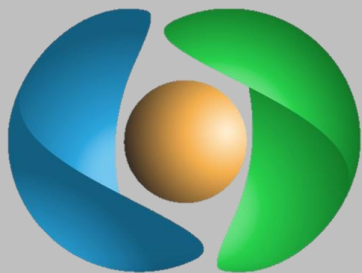
16:15 - 16:35 **reserved presentation slot**  
*to be announced*

16:35 - 16:55 **Break**

16:55 - 17:00 **Dr. Kristina Zentel & Dr. Stefan Spiegel** (Wiley)  
*Best contribution prize*

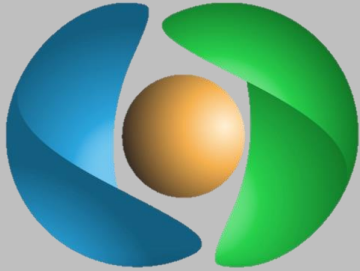
17:00 - 17:05 **Dr. Shaghayegh Hamzehlou**  
*Information on San-Sebastian workshop*

17:05 - 17:15 **Prof. Dr. Markus Busch, Dr. Kristina Zentel**  
*Farewell*



# List of Posters

| poster | poster title                                                                                                                                        | author                                                       |
|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|
| 1      | Radical polymerization of styrene in presence of recycled tires powder: experimental strategy for hybrid machine learning/phenomenological modeling | <u>C. Trinh</u> , B. Lamari, D. Meimaroglou, S. Hoppe        |
| 2      | Modeling of Copolymer Topologies in High-Pressure Ethylene Copolymerizations in 3D-Space                                                            | <u>J. Kirsch</u> , A. Weber, M. Busch                        |
| 3      | Impact of induced condensing agents on comonomer incorporation and polymer properties                                                               | <u>N. B. Ishola</u> , F. N. Andrade, T. F.L. McKenna         |
| 4      | Investigations of Mixing Behavior of Polymerization Processes                                                                                       | <u>L. Ständecke</u> , L. Dietrich, M. Busch                  |
| 5      | Kinetic of Peroxide Decomposition considering the Impact of Solvent, Pressure and Peroxide Cocktail                                                 | <u>J. Sartorius</u> , S. Albus, M. Busch                     |
| 6      | Analyses of polyacrylates using electrospray mass-spectrometry and multi-angle-laser-light-scattering (MALLS)                                       | <u>J. Mätzig</u> , M. Drache, S. Beuermann                   |
| 7      | Implementation of an Inline-NIR-Spectroscopy to a High-Pressure System                                                                              | <u>S. Hintenlang</u> , M. Busch                              |
| 8      | Inline monitoring of nanosized polymer materials using Photon Density Wave spectroscopy                                                             | <u>S. Schlappa</u> , M. Krzyczmonik, L. Bressel, M. Münzberg |
| 9      | Kinetic investigation of the Dushman reaction for micromixing time calculation                                                                      | <u>E. Arian</u> , W. Pauer                                   |
| 10     | Visualization of Relief Phenomena in High-Pressure Systems                                                                                          | <u>A. Röblitz</u> , M. Busch,                                |



# Book of Abstracts

1. Stephanie Schlappa
2. Laurence Jacob
3. Sumi Murali Nair
4. Elvis Lopes Brito
5. Sheraz Tariq
6. Hesham Abdeldaim
7. Stefan Welzel
8. Andreas Feuerpfeil
9. Elisabeth Nowotny
10. Daniela Eixenberger
11. Vida Gabriel
12. Wasif Razzaq
13. Jana Sklenářová
14. Isabel Kronshorst
15. Jakub Klimošek
16. Cindy Trinh
17. Julian Kirsch
18. Niyi Ishola
19. Laura Ständecke
20. Jana Sartorius
21. Jonas Mätzig
22. Sascha Hintenlang
23. Elias Arian
24. Aaron Röblitz





## Inline monitoring of latex-particle size distribution in emulsion polymerisation process

Laurence Jacob, Werner Pauer

University of Hamburg, Institute of Technical and Macromolecular Chemistry, Bundesstraße 45 20146  
Hamburg/Germany

The mean particle size and particle size distribution in emulsion polymerisation is still usually determined by offline analysis in diluted solutions. Interfering with the process to acquire a sample can falsify the results and lead to unwanted changes in the reaction. An inline measurement method could be more precise and less subject to problems. New investigations regarding the inline measurement method of photon density wave (PDW) spectroscopy<sup>[1]</sup> were performed to explore its suitability for inline particle size measurement in high solid content emulsion polymerisation. The objective of the experiments was to determine whether offline methods such as dynamic light scattering (DLS) and sedimentation analysis, by means of disc centrifuge, could be replaced by PDW spectroscopy. To do so, a series of high solid content emulsion copolymerisations of vinyl acetate and Versa® 10 were carried out in different reactor sizes, going up to 100 L. The emulsifier content was varied to target different particle sizes, achieving a size range of 50 to 325 nm. The reactions were carried out in a semi-batch process, using a redox initiator system, consisting of L-ascorbic acid, tert-butyl hydroperoxide and ammonium iron (III) sulfate. The results of the different methods were plotted against each other. The overall results of the method comparison showed a slope of  $(0.94 \pm 0.06)$  and a correlation quality of 98% for the linear fit comparing PDW spectroscopy with a disc centrifuge, and a slope of  $(0.99 \pm 0.14)$  and a correlation quality of 92% with DLS. The results seem very promising regarding the correctness of the PDW spectroscopy measurements and the suitability of PDW spectroscopy was proven experimentally with a polymer content of up to 63 wt%.<sup>[2]</sup>

<sup>[1]</sup> L. Bressel, J. Wolter, O. Reich, J. Quant. Spectrosc. Radiat. Transf. 2015, 162, 213–220.

<sup>[2]</sup> L. I. Jacob, W. Pauer, RSC Adv. 2020, 10, 26528–26534.

### Your notes:







**Soft Core-Hard Shell Latex Particles for Cracking Free Thick Polymer Coatings**

*Hesham Abdeldaim, José M. Asua*

*POLYMAT, University of the Basque Country UPV/EHU, Avenida Tolosa 72, Donostia-San Sebastian 20018, Gipuzkoa, Spain.*

*Hesham.abdeldaim@polymat.com, Jm.asua@ehu.es*

Due to environmental reasons, the coatings market is shifting from solvent-borne to waterborne polymers. The main hurdle to be overcome in this transition is the so-called film forming paradox of the waterborne coatings that refers to the need of achieving at the same time easy film formation at room temperature (that requires a low T<sub>g</sub> polymer) and strong mechanical properties (that need high T<sub>g</sub>). Traditionally, this has been achieved by using coalescent agents that plasticize the polymer during the film formation and later evaporate leaving a hard film. However, the use of coalescent agent is under scrutiny as it is a VOC that is released to the environment. One alternative found by the coating manufacturers has been to use heterogeneous particles comprising hard and soft polymers. Among the different particle morphologies, the soft core-hard shell structure gives the best balance. The hard shell forms a honeycomb structure that provides excellent mechanical properties. However, during the formation of the film, the hard shell should be deformed and this creates stresses in the film. The stresses increase with the thickness of the film leading to the formation of cracks.

In this presentation, the mechanisms of cracking formation during film drying will be unveiled combining carefully design experiments and mathematical modelling. It will also shown how this knowledge can be used to develop strategies to avoid cracking and enhance the mechanical integrity of the film while having a low minimum film forming temperature.

**Your notes:**

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Specialty polymers such as Polyvinylpyrrolidone (PVP) are mainly produced in batch or semi-batch operated tank reactors. The advantage of this process types is its robustness and flexibility. To produce consistent product quality, lower maintenance costs and better energy efficiency, continuous reactor systems have been considered as alternative. Especially, tubular reactors with mixing elements are of interest to manage low-volume products. A serious problem of continuous operation in mixer-reactors is the formation of fouling deposits which can result in blocking and shutdown of continuous reactors.

A prerequisite to formation of fouling deposits and wall layers are side reactions which produce high molecular weight, branched, or even crosslinked polymer chains.[1] The formation of these polymers (gel formation) occurs preferably in dead zone behind mixing elements as well as close to the wall. The locally increased residence time in such regions increase the impact of side reactions. Formation of a viscous layer at reactor walls or dead-zones changes the flow pattern, leads to large cross-sectional concentration gradients and amplifies diffusive mass transport of monomer. As large and branched polymer chain can hardly “escape” from the viscous regions due to low diffusion velocity, a highly viscous layer is built up. Such behavior has been reported for polymerization in tubular reactors, for example [2],[3],[4],[5].

The polymerization kinetic of N-vinylpyrrolidone (NVP) has been extended by side reactions. Formation of terminal double bounds was identified as the cause of high molecular, branched polymer [1]. The number of terminal double bonds are modeled with a pseudo-distribution approach and the chain length is solved directly in the original model. The proposed mechanisms has been validated against experimental data from continuously operated stirred tank reactors [6]. For CFD implementations, the original two dimensional model was reduced to a zero dimensional moment model on all discrete property coordinates to reduce the numerical effort.

To investigate the interplay between hydrodynamics, diffusive mass transport and reaction kinetics we conducted CFD simulations in tubular reactors without mixing elements and carefully compared model predictions to a comprehensive set of experiments.

The polymer properties are represented by their moments. If the diffusion coefficients for polymer, monomer and solvent are identical, transport equations for moments can be derived easily. This is here not the case. It is essential to consider the low mobility of polymer chains compared to monomer and solvent. Therefore, we used a new approach based on Maxwell-Stefan diffusion. The transport equations of moments now account for low mobility of polymer chains and high mobility of solvent and monomer. In addition, we implemented an increasing concentration-dependent viscosity. The model has been implemented into the open-source package Openfoam®. CFD simulations predict the formation of a highly viscous wall layer in a tubular reactor, which strongly depends on monomer and initiator concentration and on flow velocity.

To validate model predictions a capillary reactor was set up and the residence time distribution of experiments and CFD predictions were compared.

To determine the residence time experimentally, a salt solution was used as a tracer and measured with a conductivity cell at the inlet and outlet of the reactor. To achieve a pulsed-shaped inlet signal, a HPLC switching valve with a sample loop was used to inject the tracer.

Different experiments with varying monomer and initiator concentrations are carried out to validate the model predictions in a wide range of conditions.

An example of CFD simulations is shown in Figure 1, which presents the polymer weight fraction of different monomer concentrations after 100min of reaction time. An increase of monomer and initiator concentration causes the occurrence of a smaller layer. Simultaneously, the starting point for the formation of the wall layer can be observed with greater axial distance from the inlet. The formation of wall deposits changes the shape of the residence time distribution. The viscous layer leads to a faster breakthrough of the tracer impulse and a strongly increased tailing, which is in accordance with experimental findings.

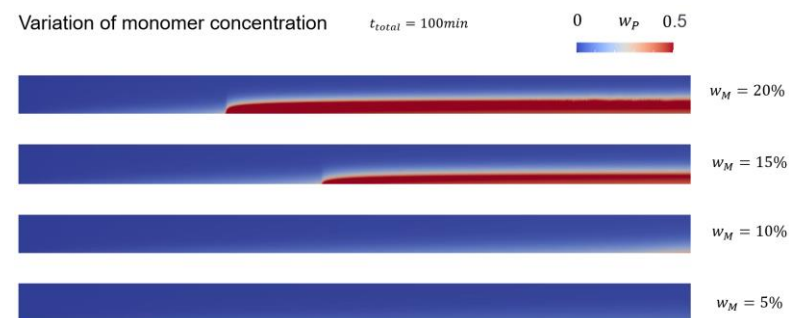


Figure 1: Polymer weight fraction for different monomer feed concentrations after 100min of reaction time.

- [1] P. Deglmann, M. Hellmund, K. Hungenberg, U. Nieken, C. Schwede, and C. Zander, “Side Reactions in Aqueous Phase Polymerization of N -Vinyl-Pyrrolidone as Possible Source for Fouling,” *Macromol. React. Eng.*, p. 1900021, Aug. 2019.
- [2] M. Hellmund, “Kinetik und Modellierung der kontinuierlichen Polymerisation von N-Vinylpyrrolidon,” University of Stuttgart, 2020.
- [3] S. Fries, D. M. Castañeda-Zúñiga, J. Duchateau, P. Neuteboom, C. T. Porras, and M. Busch, “Fouling in the High Pressure LDPE Process: Experimental and Computational Investigation Approach,” *Macromol. Symp.*, vol. 360, no. 1, pp. 78–86, 2016.
- [4] M. F. Cunningham, H. K. Mahabadi, and K. F. O’Driscoll, “Bulk polymerization in tubular reactors iii. Modelling fouling behaviour,” *Polym. React. Eng.*, vol. 1, no. 2, pp. 245–287, 1993.
- [5] S. Fries, “Modelling of Fouling Mechanisms in the LDPE Synthesis,” Technical University of Darmstadt, 2019.
- [6] C. Zander, K. D. Hungenberg, T. Schall, C. Schwede, and U. Nieken, “Modeling Strategies for the Propagation of Terminal Double Bonds During the Polymerization of N-Vinylpyrrolidone and Experimental Validation,” *Macromol. React. Eng.*, vol. 14, no. 3, 2020.









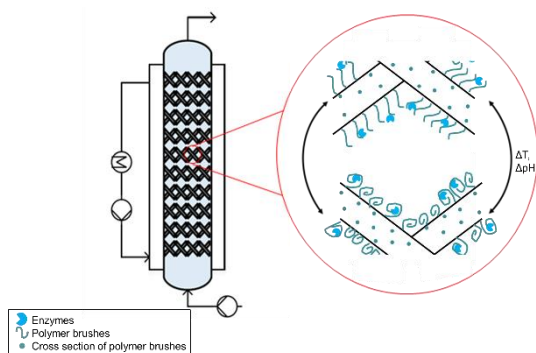
## Smart Reactors - Surface Enhancement of Additively Manufactured Structures by ARGET ATRP

*D. Eixenberger<sup>1</sup>, M. I. Maiwald<sup>2</sup>, D. Herzog<sup>2</sup>, A. Dawood<sup>1</sup>, C. Emmelmann<sup>2</sup>, A. Liese<sup>1</sup>*

<sup>1</sup> *Hamburg University of Technology, Institute of Technical Biocatalysis, Germany*

<sup>2</sup> *Hamburg University of Technology, Institute of Laser and Systems Technologies, Germany*

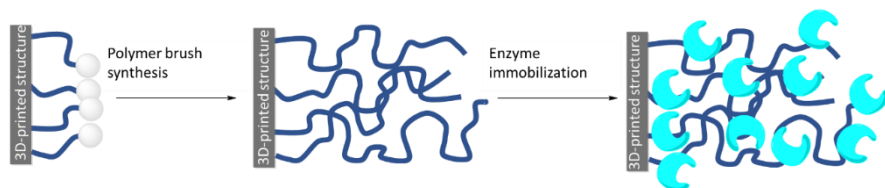
To fulfil the demands of future industry, smart reactors are essential. Therefore, additive manufacturing is a very promising technology, as it enables the production of tailor-made structures in a fast and cost-effective manner [1]. When applied in packed bed reactors, these structures can be designed in a heat and mass transfer enhancing manner, hence, to improve the efficiency of the whole process [2].



**Figure 1** Packed bed reactor with additively manufactured packing. Surface enhancement by stimuli responsive polyacrylic acid brushes including subsequent enzyme immobilization

Due to low porosity of the additively manufactured material, an application as heterogeneous biocatalyst support is uneconomic. To enable a higher surface per volume ratio, ARGET ATRP (Activator ReGenerated by Electron Transfer Radical Polymerization) is applied for polymer brush synthesis on 3D-printed material. A schematic overview of the surface enhanced additively manufactured structure, with immobilized enzymes, is shown in Figure 1.

The chosen support material is Nylon 12, as there are trivial surface functionalization procedures known. Besides FTIR spectroscopy (Fourier Transformation Infrared Spectroscopy), also XPS (X-Ray Photoelectron Spectroscopy) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) are performed to determine the covalent binding of initiator to the surface qualitatively and quantitatively. Finally, the attached polymer is analysed via TGA (Thermogravimetric Analysis), SEM (Scanning Electron Microscopy), FTIR and XPS. Figure 2 summarizes the functionalization procedure of a 3D-printed structure to yield surface



**Figure 2** Workflow of surface enhancement on additively manufactured structure with subsequent enzyme immobilization

Further optimization of the polyacrylic acid synthesis in free solution is targeted by a response surface plot, using a Box-Behnken Design. Factors accounted for are, the catalyst amount, reducing agent, time and the volume of organic solvent.

Moreover, a correlation between monomer conversion and molecular weight of polymer brushes is of utmost importance, to determine the influence of molecular weight on the residual enzymatic activity. This approach is demonstrated in aqueous media applying a hydrolysis reaction catalysed by the Esterase 2 from *Alicyclobacillus acidocaldarius*. Finally, the synthesis of stimuli responsive polymer brushes not only tackles the limitation in surface area but moreover, it implements the possibility of an autonomous process control by presence of certain stimuli. For instance, a shift in pH causes a conformational change of the polymer brushes (coil-globule transition) what affects enzyme activity by diffusion limitation. This effect enables an autonomous process control by adapting to continuous changes of process conditions during the reaction progress.

### References:

- [1] Hübner, Eike G.; Lederle, Felix (2019): Spezielle labortechnische Reaktoren: 3D-gedruckte Reaktoren. In Willi Freeden, Reiner Rummel (Eds.): Handbuch der Geodäsie, vol. 2. Berlin, Heidelberg: Springer Berlin Heidelberg (Springer Reference Naturwissenschaften), pp. 1–29
- [2] Büscher, N., Spille, C., Kracht, J., Sayoga, G., Dawood, A., Maiwald, M., et al., Countercurrently Operated Reactive Extractor with an Additively Manufactured Enzyme Carrier Structure, *Org. Process Res. Dev.*, 2020, 24, 1621–1628

### Your notes:

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## How to increase the selectivity of the triboelectric separation of plastic waste?

*L. Kolářová, B. Tučková, J. Sklenářová, S. Jantač, J. Kosek  
UCT Prague, Dept. of Chemical Engineering, Technická 5, 166 28 Prague 6, Czechia*

Plastic materials find their use in many applications such as packaging, automotive, construction and electronic industry. This produces large amounts of plastic waste, which accumulate in landfills and the oceans. The separation of plastic materials is crucial in the recycling process to produce new high-quality materials, but moreover, separation is important even in incineration, which can be used instead of recycling. By incinerating the plastic waste, we could reduce the large volume of solid waste and we could get energy from the plastics. In other words, we can make from useless and cumulating waste a resource with a positive economic value. However, halogenated plastics (mostly PVC) cause problems during incineration because they can produce toxic gases, including dioxins. Thus, special incineration conditions are required, and then the process becomes more complicated, and incineration is no longer profitable. Therefore, the separation of halogenated plastics could be the first-step solution. Even though many separation techniques are known, they all have significant drawbacks; thus, none can be used universally. In our research, we are focusing on the improvement of efficiency of a triboelectric separation of plastics, which is a method with the potential to become an important member of the recycling chain for many reasons, such as low costs of the separation process, automatization potential, possible separation of black materials etc.

Triboelectric separation is based on the phenomenon that each plastic material obtains a different electrostatic charge by friction contact against a proper counter-material. The basic separation process consists of three main steps. In the first step, plastic waste is grinded into small pieces, in the second step, the charge is generated on their surface. Lastly, the pieces are separated during the free fall between electrodes in the electrostatic separator. The charge is 'generated' on the surface of the pieces during their contact and friction and after their subsequent separation. The amount and direction of the transferred charge are generally determined by the properties of both contacted objects, i.e., grinded waste particle and the charging cell made from a specific counter-material. The selection of a counter-material is the most challenging task of designing a triboelectric separator, as it plays a key role in the controlling of the charge obtained by individual plastic pieces. The tribocharging of dielectrics or insulators is not well understood yet, although some theoretical or empirical concepts correspond well with experimental results. So even determining a suitable counter-material is not possible. Thus, there is no sufficient knowledge to predict the charging behaviour of such similar materials like plastics when distinguishing between their grades (for example, HDPE and LDPE), and that is why most of the work needs to be done experimentally. Furthermore, the nature of the materials is not the only parameter influencing the direction and magnitude of the transferred charge, but the type of contact of pieces with the counter-material, the properties of the surrounding atmosphere, as well as the dimensions and the shape of the grinded pieces also plays a role.

We use self-constructed charging apparatus based on different contacting approaches: contact during rotational motion, enhanced by vibrations or contact during sliding motion. To evaluate the charge on pieces, we use two methods: we can estimate the total charge in a sample in a Faraday pail connected to the electrometer (used for experiments with pure materials, not mixtures), or we are using our self-constructed free-fall separator to evaluate the charge distribution in the sample. After the separation, plastic pieces are collected in boxes based on the trajectory of their fall in the electric field. Then, the charge of pieces in individual boxes is measured in the Faraday pail. Finally, the representation of different plastic materials in collectors is evaluated.

Our work is focused on improving electrostatic separation by finding proper counter materials to effectively separate multiple-component plastic mixtures by separating one material per cycle and recharging the remaining mixture with different counter materials during each cycle. We compared the most promising tribocharging mechanisms for automatization (rotational and vibrational), and we combined these methods with a corona discharge to decrease the time needed to achieve sufficient, i.e., saturation charge on individual pieces. We performed a study addressing the charging dependent on material composition with 8 cells with different compositions and 9 waste plastic materials, and we showed that the magnitude and, in some cases, even polarity can be controlled by the choice of the cell material and the mode of charging. These results can be used as guidance to choose a suitable material for the efficient separation of various plastic mixtures, as we demonstrated with the separation of 3-component mixtures, aiming for the successful separation of halogenated material – PVC from the mixture, as PVC is inconvenient for incineration. We began with a one-stage separation with high purity of the two materials but in a low yield, and then we introduced the repeating cycle in two different ways. One is to reach higher purity by separating only one material in one stage, and another one aims to increase the yield. Finally, we reached to sort out the PVC with purity up to 91 % at 88% recovery, PET of 77% purity and 64% recovery and completely PVC-free, and PP of 75% purity and 80% recovery with approx. 3 % of PVC.

In our further experiments, we focus on the effect of an external electric field, which can be used to fine-tune the charging of plastic particles during tribocharging. Our results show that with the increasing field strength in the charging cell, we can lower the value of the saturation charge of particles. By controlling the saturation charge of particles by an external electric field, we could decrease the number of charging cells consisting of different materials needed to efficiently separate a mixture of plastic waste and thus, simplify the automatization of the process.

**Your notes:**

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## Kinetic of Peroxide Decomposition considering the Impact of Solvent, Pressure and Peroxide Cocktail

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Peroxides possess a labile oxygen-oxygen bond which can split homolytically forming radicals induced by heat, pressure or radiation. Due to their decomposition, peroxides are applied as initiators for radical polymerisation. Therefore, their kinetic is a crucial part to understand and model these processes. Heating peroxides in a non-reactive solvent, their kinetic of decomposition can be investigated separately from polymerisation reactions.

LDPE is a broadly utilized polymer for numerous applications and produced using radical polymerisation on industrial scale. With pressure up to 3000 bar and temperature up to 300 °C, the handling and research of this process is a challenging task [1]. Due to the harsh conditions, reliable process near data is scarce. Buback [2] and Luft [3] investigated the kinetic of peroxide decomposition using IR measuring the increase of intensity correlating to a concentration increase of decomposition products. As a result of their temperature and pressure dependency, kinetic parameters such as activation energy, the reaction rate constant and activation volume can be evaluated. This optical setup is limited to low-viscous media showing transmission and can be handled in a flow cell. Therefore, the high-viscous conditions at the end of the polymerisation process are not accessible. Using high-pressure calorimetry for kinetic investigations this gap is tried to be filled.

The peroxide decomposition is highly exothermal causing intense heat flux and therefore calorimetric signals. The time-dependent enthalpy of decomposition contains its kinetic information which can be analysed by the Borchardt-Daniels method or thermokinetic software like THINKS [4]. The transitiometer enabling simultaneous control and recording of temperature, pressure and volume up to 3000 bar and 400°C is the mainly used device. Its isobaric mode allows investigations of pressure dependency and its pressuring system of solids and liquids including high-viscous media.

### Influence factors

Former research focuses on the decomposition of peroxides in unpolar, low-viscous solutions of heptane or isododecane reflecting the chemical environment of ethylene. In consequence of the increasing viscosity during polymerisation progress and the variety of (co-)monomers, a broader range of physical properties should be represented by different solvents. Therefore, acetone, ethylbenzene, heptane, squalane and LDPE as matrix is investigated as solvent. An increase in viscosity limits the molecular freedom of movement leading to a higher energy demand for translation motion and therefore a higher decomposition temperature.

Like the cage effect is caused by high viscosity, pressure can also change the mobility of molecules. The pressure effect on kinetic is expressed by the activation volume calculated from the pressure dependency of the reaction rate constant. The performed isobaric temperature scan between 100 bar and 2000 bar meets observation from Buback.

The chemical environment of peroxides can be influenced by the presence of another peroxide or its decomposition products. The use of peroxide cocktails is common for polymerisation starting the reaction smoothly, influencing the polymer properties and serving different stages of reaction but they are not investigated as a mixture in literature. In experiments a mixture of two peroxides decomposing at different temperatures shows a shift of kinetic parameters and decomposition temperature compared to the single peroxide.

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- [2] M. Buback, L. Wittkowski, *Zeitschrift für Physikalische Chemie*, **1999**, 210, 61-81.
- [3] G. Luft, *Chemie in unserer Zeit*, **2000**, 34, 3, 190-199.
- [4] <http://www.thinks.chemphys.ru/shiny/Redir/>, 15.10.2021.

### Your notes:

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## Visualization of Relief Phenomena in High-Pressure Systems

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The design of pressure relief systems, such as those used in the high-pressure polymerization process, is usually done using regulations based on single-phase flows, such as API 520 [1]. In this context, the mass flow discharged in the event of relief is of central importance, since it determines the required relief cross-section. This mass outflow is essentially affected by the density of the ventilated medium as well as the valve characteristics. The required relief cross-section varies depending on the flow present. For example, the assumption of a single-phase flow leads to relief cross-sections that are too small when a two-phase system is relieved. Accordingly, an understanding of the relief characteristics of two-phase flows and consideration of the changing properties is essential for the design of safety devices.

A 34 mL view cell is used to visually analyze the relief from the high-pressure region. The image acquisition is done with a high-speed camera to show the occurring phenomena in detail. In addition, the temperature and pressure changes can be recorded via a fast measurement sensor system. For a more detailed investigation of the outflow characteristics of two-phase flows, various test parameters can be varied, such as the process conditions, the relief position and the nozzle length. The discharge takes place at a pressure of 2000 bar and different initial temperatures. Vinyl acetate is used as the comonomer, with the proportion being varied. The relief process itself is realized by a pneumatic diaphragm valve. High-pressure lines are used as the nozzle, the inner diameter and length of which can be varied so that the relief speed can be influenced.

An isentropic nozzle model according to J. Schmidt [2] is used to determine the relief velocity considering the different conditions and varied parameters. The model can be applied up to the point where phase separation occurs during expansion since the expansion process follows an isentropic behavior up to this point. In the further course, a two-phase flow must be assumed, whereby further factors must be considered. This is realized by the HNE-DS model of J. Schmidt [3]. The characterization of the boiling delay factor included in the calculation is enabled by the visualization of the relief process. This research intends to be able to simulate the relief process for single-phase as well as for two-phase flows, based on the isentropic nozzle model [2] as well as the HNE-DS model [3], to improve the design of safety devices.

[1] G. Luft et al., *Chemical Engineering Technology* 30, 695-701 (2007).

[2] J. Schmidt, W. Peschel, *Process and Plant Safety*, 71-77 (2012).

[3] J. Schmidt, *Forsch Ingenieurwes* 71, 47-58 (2007).