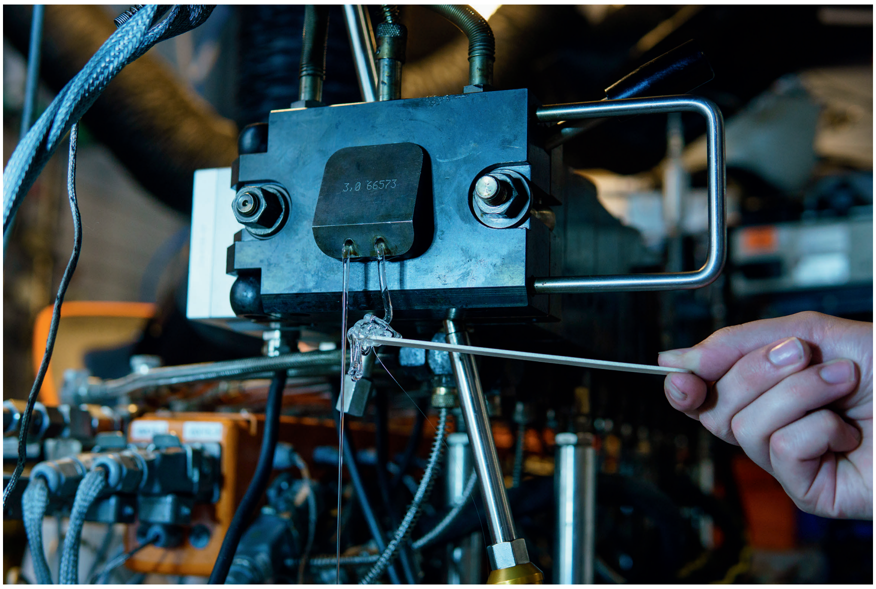
Reactive Extrusion of TPU

Production of Thermoplastic Polyurethanes with Reduced Carbon Footprint

The simple replacement of petroleum-based components with renewable alternatives in a well-established reactive extrusion process is a promising route to more environmentally friendly thermoplastic polyurethane elastomers (TPU). However, this requires a comprehensive understanding of the interactions between chemical reactions and material flow within an extruder, as well as a thorough understanding of the effects of heat and shear on polymerization and melt processing.



Extruded strand from the continuous synthesis of a thermoplastic polyurethane, containing the new paraformaldehyde-based polyol © Fraunhofer ICT

Driven by the strategy of circular economy, the sustainability of polyurethanes (PU) – both in terms of chemical composition and production technologies – has also become an important issue in the polymer industry. One promising approach to reducing the CO_2 footprint is the efficient replacement of precursors derived from fossil sources with renewable materials. In the "Dream Polyols" project, a consortium including Fraunhofer ICT has addressed this issue by replacing the core of a standard polyether polyol with a paraformaldehyde block (pFA), resulting in a triblock structure with a potentially significant content of renewable raw materials.

The use of pFA from renewable sources opens a path to chemical intermediates that consist entirely of building blocks derived directly or indirectly from CO_2. These newly synthesized triblock polyols have been tested for their suitability in a range of PU end products such as foams, adhesives, elastomers and thermoplastics. Fraunhofer ICT established a production process – reactive extrusion (REX) – to use the new, sustainable components in the manufacture of thermoplastic polyurethane elastomers (TPU).

Advantages of Reactive Extrusion

The REX process is superior to most polymerization methods due to its versatility and economic advantages. In REX, the raw components are continuously fed into the extruder and reacted at elevated temperature under shear. The possibility to completely avoid the use of solvents is a notable environmental advantage.

REX is particularly suitable for the production of TPU systems, but it requires a high degree of process control to consistently achieve the desired product quality. This is due to the complex relationship between the progress of the reaction and the properties of a flowing melt with a constantly changing viscosity. Under these circumstances, finding the processing window suited to the properties of the reactive components requires a deep understanding of the chemical reaction sequence and a process engineering perspective. Since the pFA-based polyol was only available in small quantities at the beginning of the project, commercial reference materials (standard polyols) were initially used for the development steps.

Novel Polyol in Classic TPU

The triblock structure of the developed polyol consists of a new pFA core end-capped with chains of polypropylene oxide (PO), which is a typical PU building block. To observe how the substitution of a PO segment by a more renewable building block influences the performance of PU materials, Fraunhofer ICT first carried out a laboratory investigation. A comprehensive material study showed the field of application of the new polyol and its effect on the thermal and mechanical behavior of the resulting TPU products (**Fig. 1**). This made it possible to determine the ratio between the raw components required for PU synthesis (polyol, chain extender and diisocyanate), which has a decisive influence on product quality. On the basis of this material composition, a REX process was developed for continuous production of the selected TPU material on a pilot scale (**Fig. 2**). »

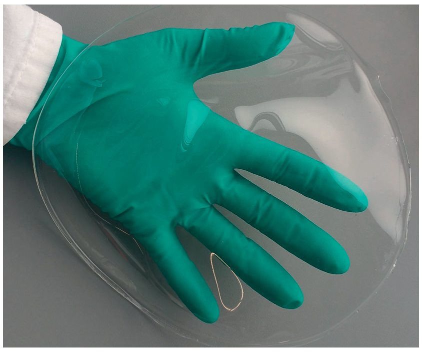


Fig. 1. Thermoplastic polyurethane synthesized using the newly developed polyol based on paraformaldehyde core. The solvent cast foil has excellent transparency © Fraunhofer ICT

From the REX Concept to the Pilot Process

In the initial phase, the stability of throughput and conversion was the focus of development (**Fig. 2b**). This process was divided into three main elements: tailoring the set-up for dosing the raw materials, design of the screw construction and definition of a temperature gradient along the continuous reactor. The use of a modularly designed co-rotating twin screw extruder, which is available at Fraunhofer ICT (manufacturer: Leistritz, Nuremberg, Germany; type: ZSE 18 Maxx with 18 mm screw diameter, L/D = 60 and 15 heating zones), allowed significant flexibility in terms of the process parameters applied and the residence time. Kilogram quantities of raw materials are required for the development steps of a reactive process on a pilot scale. The basic investigation was therefore carried out with commercially available PO-polyol, which is comparable in structure and processing behavior to the novel triblock polyol (**Fig. 2a**).

In the case of TPU production, the correct stoichiometric ratio of the raw components is crucial to building long molecular chains and obtaining a high-quality product. For this reason, special emphasis was placed on adjusting the precise feeding of the premixed raw materials (**Figs. 2b, 3a and 3b**), to avoid any process instabilities. Each raw material was fed through a separate dosing system, which was tailored to the required viscosity, throughput and temperature conditions. The material flows were combined before entering the extruder port.

The temperature profile along the length of the extruder was designed for the steadily increasing viscosity of the polymerizing material up to the fully reacted product. A uniform flow in the initial zones of the extruder is of crucial importance in maintaining the homogeneity of the fast-reacting mixture. The temperature was adjusted to the viscosity of the premixed raw components, which is determined by the polyol. This allows an efficient transport of the reactants and the advancement of the PU reaction. The increasing temperature gradient in the subsequent sections was designed to complete the polymerization and melt the TPU produced. The targeted setting of the temperature profile protected the reacting components from thermal degradation and side reactions, resulting in a high conversion rate and a polymer with the desired properties.

The screw configuration combined elements with high and low conveying capacity, thus providing sufficient residence time for complete polymerization. The design and position of high-shear zones is critical for effective mixing of the reacting components to reduce the risk of degradation. Shear segments were installed to increase the local filling level in extruder zones where there was moderate reaction conversion, and thus regulate fluctuations in the flow caused by significant viscosity changes (**Fig. 3b**). Such instabilities result from the alternation between states of high and low conversion, and are typical for polymerization in the extruder. They manifest themselves as fluctuations in machine torque and material flow at the die. A targeted adjustment of the screw design, the temperature profile and the mixing speed in iterative steps takes into account the interactions between the chemical reactions and the material flow. By optimizing the interconnected parameters, REX achieves a stability level comparable to that of conventional compounding (**Fig. 3c**).

Use of Sustainable Polyols in the Established REX Process

Based on an optimized REX parameter set, the material quality was thoroughly investigated in the subsequent develop-

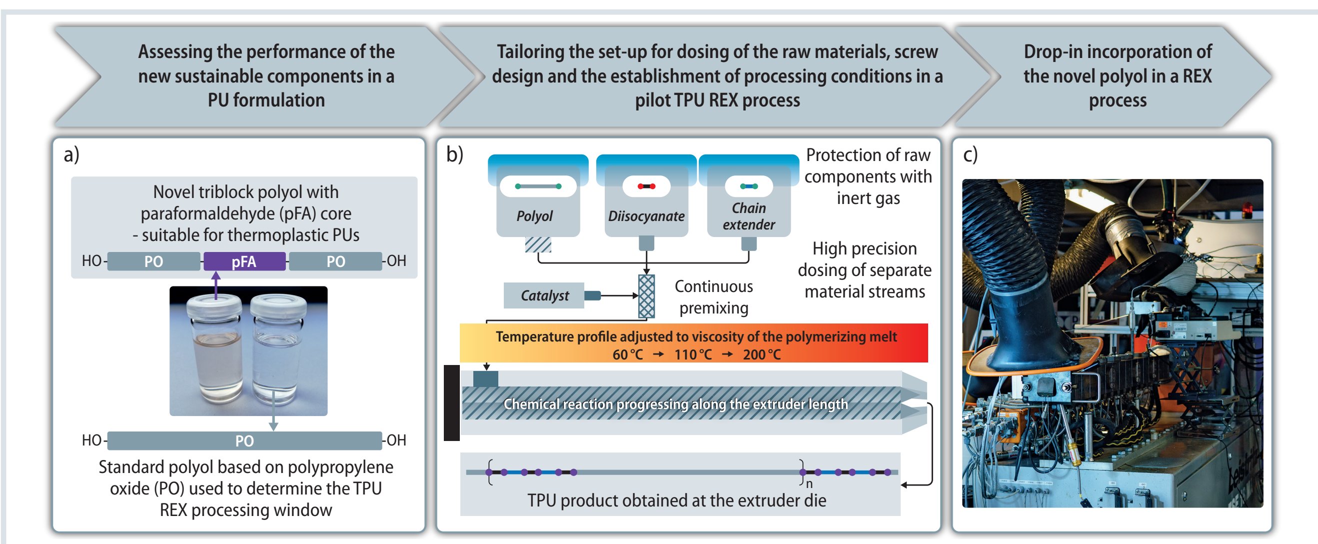


Fig. 2. Development steps within "Dream Polyols": from the preliminary determination of the polyurethane formulation (a) and the REX conditions (b) to the implementation of newly developed components in the established processing approach (c) Source: Fraunhofer ICT, graphic © Hanser

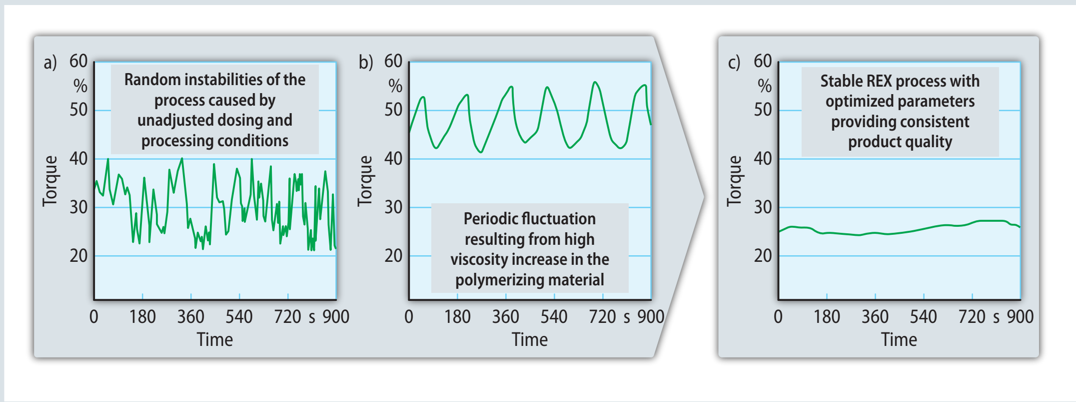


Fig. 3. Determining the physical and chemical causes of the instabilities in reactive extrusion allows the dosing strategy (a) and the processing window (b) to be adjusted, resulting in a well-controlled process (c) © Fraunhofer ICT

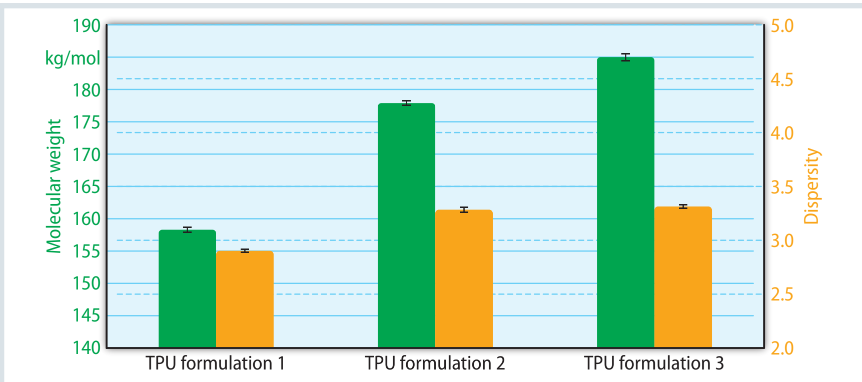


Fig. 4. Molecular weight and dispersity of thermoplastic polyurethane produced by the REX process. The polymer performance is controlled by a simple adjustment of the material formulation Source: Fraunhofer ICT, graphic © Hanser

ment phase. During the extrusion experiments, the TPU product was collected at the extruder die for direct spectroscopic measurement in order to estimate the material conversion. The absence of the isocyanate band in the spectra confirmed that the residence time is suitable to complete the polymerization process to a high degree. In order to achieve optimum product properties, the TPU formulation developed in the laboratory step was further adapted to the conditions of the pilot production. The high dosing accuracy of the raw materials facilitated the screening of the stoichiometric ratio between the reactants. The flexible change in the throughput of the diisocyanate component by small increments altered the processing behavior and the molecular weight of the resulting product (**Fig. 4**).

Knowledge of the critical parameters made it possible to conduct a complete REX feasibility study using only a few kilograms of the newly developed polyol (**Fig. 2c**). The TPU materials produced were transparent, flexible solids with no signs of material inhomogeneity. The quality of the REX pilot process with the novel pFA-based polyols demonstrated the drop-in solution for their implementation in an existing production process.

Conclusion

Using one of the most versatile processing tools – the extruder – for the continuous synthesis of polymer products brings intrinsic technological and ecological benefits. Its application in the production of high-quality plastics based on CO_2 sources is a simple path toward a "green" polymer industry. The "Dream Polyols" project demonstrated the combination of both approaches in the development of new, sustainable components for the polyurethane market. A particular advantage at the development stage and in controlling the quality of industrial REX production could be achieved by applying advanced process monitoring and automation. The integration of online characterization technologies available at Fraunhofer ICT, such as viscometry, near-infrared or Raman spectroscopy, enables rapid feedback on the local progress of the reaction and the material condition. The development of a methodology for simple online characterization in the extruder, which is currently being carried out at Fraunhofer ICT, is therefore an indispensable step to further simplify the optimization of REX processes. ■

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Acknowledgments

This work was carried out as part of the project "Dream Polyols" (funding code: 03XP0052C), which is partly co-financed by the German Federal Ministry of Education and Research (BMBF) within the research program "MatRessource – Materials for a resource-efficient industry and society". The authors would like to thank the Project Executive Agency in Jülich, Germany, for supporting the project, and the consortium leader Covestro.

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