Polyurethanes with components made of renewable resources and recyclates

Dr. T. Anders
Fraunhofer Institute for Chemical Technology
Department Environmental Engineering
Project Team Leader Polymers and Additives
D-76227 Pfinztal
Germany

ABSTRACT
The Fraunhofer Institute for Chemical Technology (ICT) is part of the Fraunhofer-Gesellschaft, which is the largest research organization in Europe. In the department of Environmental Engineering new sustainable products and processes are developed and investigated. Selected research topics will be presented concerning the development of polyurethanes, including sustainable components from renewable resources and recycling materials.

INTRODUCTION

In collaboration with partners from industry, academia and public organizations all over Europe the department of Environmental Engineering of the Fraunhofer ICT works *inter alia* on the development of Polyurethane (PU) components from renewable resources and recycled materials. This paper will briefly present polyurethanes prepared with components made of renewable resources and recycling materials.

THE USE OF WOOD WASTE MATERIALS

The scope of the EU project Grease was to investigate and develop processes to convert high value products from low-value forestry byproducts. Therefore partners form pulp and paper industry worked together with bio-refinery industry, PU industry and research organizations to exploit a novel lipid platform towards sustainable bio-based products through multi-functional fatty acids.[1]

The conventional process of wood in the pulp and paper industry, which converts approx. 403 million tons 2013 worldwide, starts with segmentation of tree trunks in to 3 m length.[2] After storing the tree trunks are debarked and chipped before the pulping process. 1000-3500 tons per day of pulp (about 50 wt.% of the dry wood) are produced in modern digesters.[3] Beside the bark the main byproduct of this process is the black liquor, which is a basic aqueous solution containing salts, tall oil, lignin and hemicellulose. While the pulp is further processed to products usually the byproducts are used in low-cost applications. The tall oil soaps are skimmed of the black liquid, than acidified to produce crude tall oil (CTO). From pines the average yield of CTO is 30–50 kg/t pulp and consists of rosin acids and tall oil fatty acids (TOFA). Globally about 2 million ton/year of CTO are refined.[4] The rest of the CTO, bark, lignin and hemicellulose are typically used for energy recovery.

The aim of the project was to generate high value products from birch bark and CTO, which are waste materials in process of pulp preparation. For the bark several extraction and chemical conversion processes were investigated and evaluated in order to yield betulin and suberin fatty acid fractions. In addition CTO was purified to highly pure TOFA and converted to different chemical building blocks, which find their application as cross linkers, monomers for polyester and polyol synthesis and other oleochemical based products.

Those materials from wood waste were tested in several products like bioactive fine chemicals, coatings and adhesives, bioplastics and polyurethane materials. These materials featured in polyesters and polyols for polyurethanes.

Rigid PU foam was prepared with suberin fatty acid polyester polyols, which have a bio-based polyol content of 100%. TOFA was functionalized by oxidation reactions to monomers for polyester polyols. Those bio-based polyester polyols were used in formulations for rigid PU foams with content of 60 wt-% bio-based polyol and in formulations for PU elastomers with content of 50-95 wt-% bio-based polyol. The PU products prepared by the presented wood waste materials showed similar properties to standard products. A disadvantage of the PU products is the light up to strong brown color.

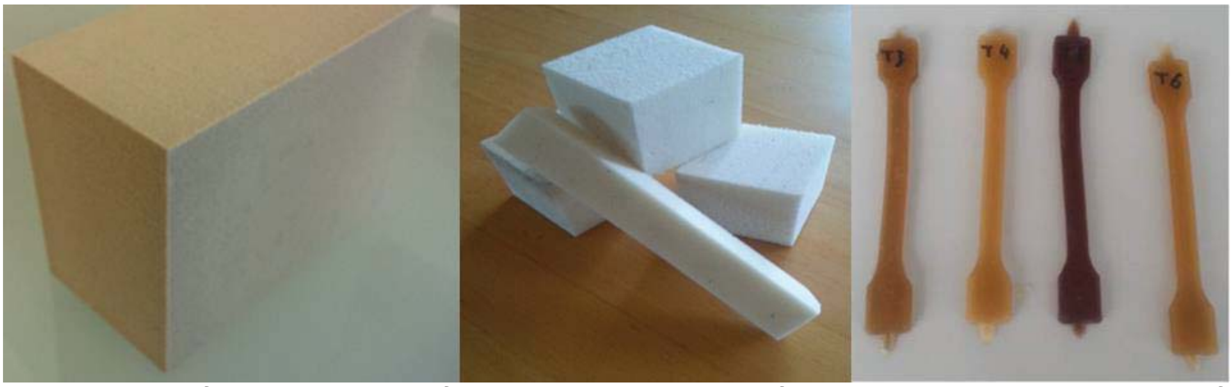

Figure 1: From left to right: Rigid PU foam prepared with suberin fatty acid polyester polyols; Rigid PU foam prepared with polyester polyols prepared from TOFA; PU elastomers containing polyester polyols prepared from TOFA (pictures provided by Rampf).

The project showed the successful use of wood waste materials in PU products. The chemical processes were done in small pilot scale and products were achieved in kg amounts. The developed processes showed potential to be up-scaled into industrial interesting scale.

By using waste materials for PU product preparation the whole process chain might become economically and ecologically more efficient. First feasibility studies showed scenarios where the implementations of the investigated processes are of commercial interest for project partners. Further work has to be done on fine tuning of the processes, evaluation of business cases and LCA of the howl process chain.

THE USE OF FLEXIBLE FOAM WASTE MATERIALS

PU flexible foam production volume in EU is about 750.000 t/a; tendency is increasing. During processing of the PU foams into products like seating, mattresses etc. up to 30% of the material are production waste. Usually those waste materials are used for energy recovery or recycled as regrind for low-value products. Chemical recycling of PU products is gaining more and more industrial attention. Today most known and used solvolysis methods are alcoholysis (e.g. glycolysis) and acidolysis.

2013 an exemplary project showed investigation and developments in the field of acidolysis and recycling of PU, ending in an industrial scale plant for the recycling of PU foam components.[5,6] Starting 1992 with basic investigations on acidolysis process of PU and first positive foam experiments with the university of applied science in Aalen (Germany), the acidolysis was continuously improved and tested for MDI-acoustic foams (1996), TDI-hot molded foam (1997), various TDI/MDI- molded foams like cushions and head rest (1999-2006). 2007 was first automatic processing in flexible slap-stock foam technical center (Evonik and Hennecke) and 2011 initial operation of a 7 ton acidolysis with 7 ton capacity (Rampf Eco Solutions and Keil Anlagenbau). In the following years first industrial pre-production development of secondary polyols and material incorporation in PU mattresses formulation were successfully done (Metzeler).

Typically secondary polyols have slightly higher OH-values, acid values, water content and viscosity than standard polyols for flexible foams. So up to 20 % of polyol component could be exchanged by secondary polyols without effecting mechanical properties like compression resistance and compression set of the resulting PU foam block.

Properties	Polyether polyol Voranol CP3322	Secondary polyol MDI-molded foam	Secondary polyol TDI-flexible slab-stock foam
OH-value [mg KOH/g]	48	54	56
Acid value [mg KOH/g]	<0,05	3	1,5
Water content[%]	<0,1	0,18	0,23
Viscosity [mPas/25°C]	500-600	3240	3180

Figure 2: Example of a secondary polyol (provided by Rampf) and comparison of properties from different example polyols.[5,6]

Optimization of the azidolysis process made it possible to produce and use secondary polyols in ton scale for industrial use. The sustainability of the secondary polyol production and its incorporation in flexible PU foam formulation for mattresses was evaluated by ecological and economical life cycle analysis (Karlsruhe Institute of Technology, Germany). The acidification potential of a secondary polyol produced by the acidolysis can be reduced up to 16% compared to production of a primary polyol (100%). The global warming potential can be reduced to 18%, the eutrophication potential reduced to 24%and the cumulative fossil energy input to 17%.[5,6] Beside those ecologically advantageous results, the economic impact is also attractive. Standard polyol price of about 1,80 €/kg compared to costs for secondary polyols of about 0,94-1,14 €/kg show, that replacing parts of fossil based polyols with recyclates is cost efficient.

BIO-BASED PU FOAMS FOR IMPROVING ENVIRONMENTAL IMPACT IN AVIATION

Clean Sky is the most ambitious aeronautical research programme ever launched in Europe.[7] Its mission is to develop breakthrough technologies to significantly increase the environmental performances of airplanes and air transport, resulting in less noisy and more fuel efficient aircraft, hence bringing a key contribution in achieving the Single European Sky environmental objectives.

The practical goals for 2020 (compared to 2000) are:

- reduce fuel consumption and CO_2 emissions by 50% per passenger kilometer
- reduce NOx emissions by 80%
- reduce perceived noise by 50%
- make substantial progress in reducing the environmental impact of the manufacture, maintenance and disposal of aircraft and related products.

The Advisory Council for Aeronautics Research in Europe has identified the main contributors to achieving the above targets. The predicted contributions to the 50% CO_2 emissions reduction target are:

- Efficient aircraft: 20-25%
- Efficient engines: 15-20%
- Improved air traffic management: 5-10%

The development of an economically and ecologically improved aircraft is an important and challenging task in this project. Therefore one main coordination task is Eco-Design.[8] Eco-Design will coordinate research geared towards high eco-compliance in air vehicles over their product life. An example of sustainability in aircraft interior is the development of green flexible PU foam which is 22 wt.-% from bio-based resources. The use of bio-polyol in PU formulation is not only improving the ecological impact of the material, but also increasing flame resistance. Green seating cushions were prepared from the material for demonstration.[9]

Figure 3: From left to right: Green PU seating cushion (Heat rest), Samples from Green PU foam bevore and after FAR 25.853 test, Aircraft seat bench with green PU seating cushion.

The project is currently ongoing. Next steps will contain recycling, long term stability testing and LCA.

CONCLUSIONS AND OUTLOOK

The successful implementation of PU components from renewable resources and recylates were demonstrated. Regarding past and recent developments on sustainable resources use and sustainable process steps and routes, the future will yield higher variety in raw materials and processing methods. So beside individual products the competence and technologies in using different types of resources in a sustainable way is of growing interest for companies.[10]

ACKNOWLEDGEMENT

The author thanks the Federal Ministry of Education and Research for the financial support of the development of an integrated process for sustainable production of slab-stock foams for the furniture, transport, construction and packaging sectors and Trial of sustainable production and utilization of PU flexible foam in pilot production (BMBF support code: 01RI05070, 01RI0907A). Thanks to the Federal Ministry of Food and Agriculture for the financial support in the project Grease: A novel lipid platform to sustainable bio-based products from low-value forestry streams through multi-functional fatty acids (BEMEL support code: 22020311). Thanks to EU support code: CSJU-GAM-ED-2008-001for founding Cleansky. Special thanks to all our collaborating project partners.

REFERENCES

[1] Further information about the Grease project at www.fnr.de; www.woodwisdom.net

[2] RISI, Annual Review of Global Pulp & Paper Statistics **2014**, http://www.risiinfo.com/pulp-paper/ppippw/Reports-RISI-2014-Annual-Review-of-Global-Pulp-Paper-Statistics-Global-Pellet-Demand-Outlook.html, (25.02.2015)

[3] J. Woodman, Pollution Prevention Technologies for the Bleached Kraft, Segment of the U.S. Pulp and Paper Industry, U.S. Environmental Protection Agency, **1993**, p. 66.

[4] J. Gullichsen, H. Paulapuro, Chemical Pulping, Papermaking Science and Technology 6B. Finland, **2000**, pp. B378-B388.

Fraunhofer ICT

[5] Further information about the project first module at http://www.nachhaltige-innovationen.de/de/473.php and http://www.cleaner-production.de
[6] U. Fehrenbacher, M. Hohenhorst, M. Kugler, M. Werth, G. Giesker, K. Schäfer, „Nachhaltige Herstellung und Verwertung von PUR-Blockschaum“, presentation at the FSK annual meeting in Essen Germany, 2012.
[7] Further information about the project cleansky at http://www.cleansky.eu
[8] http://www.cleansky.eu/content/page/clean-sky-achievements
[9] http://www.cleansky.eu/content/page/eco-design-2
[10] http://www.marketsandmarkets.com/PressReleases/Green-and-Bio-Polyols.asp

BIOGRAPHY

Dr. Anders studied chemistry at the RWTH Aachen University. During his studies he completed a semester abroad at the University of York (UK) and an internship at BASF Coatings in Münster (Germany). He achieved his PhD in Polymer Chemistry at the DWI - Institute for Interactive Materials (group of Prof. M. Möller) in the field of biological active hydrogel coatings. In 2012 he became project leader at the Fraunhofer ICT and since 2014 team leader of the project group polymers and additives in the department of Environmental Engineering (led by R. Schweppe).