CHEMICAL RECYCLING OF POST-CONSUMER MATTRESS MATERIALS

R. Hanich

Fraunhofer Institut für Chemische Technologie ICT, Joseph-von-Fraunhofer Straße 7, Pfinztal, e-mail: ronny.hanich@ict.fraunhofer.de

Keywords: chemical recycling, polyurethane, circular economy

1 Introduction

Polyurethane (PU), with an annual production of 18 million tonnes, is the sixth most produced plastic in the world, and has a variety of applications due to the wide range of raw materials used [1]. Approximately one quarter of the PU produced worldwide is used in the production of flexible foam materials such as mattresses, pillows and seating cushions for the automotive and aircraft industry.

After an average lifespan of 10 years, 30 million mattresses reached their end of life in Europe in 2017, which means an estimated volume of 450,000 tonnes for mattresses.

Currently 40 % of these are incinerated, and 60 % are landfilled [2, 3].

Starting Situation 2015:	Aims in 2019
• In EU > 60 % bulky waste landfilled • Different urban waste recycling quotes: • 70 % Belgium to 5 % Turkey • Seasonal fluctuation	• Reduction of up to 50 % of the total bulky waste currently landfilled • Production of renewable polyols: final mechanical properties not lower than 10 % and total cost saving of at least 6 % compared to virgin material • Reduction of CO_2 emission of about 20 %

Due to the EU waste hierarchy and the UN's Sustainable Development Goals 2015, the mechanical and chemical recycling of these PU materials and other plastics is attracting increasing industrial interest. The products of the chemical recycling of mixed flexible post-consumer PU waste can currently substitute up to 50 % of virgin polyol raw materials for the production of rigid foams, which come from crude oil sources. This means that the chemical recycling process is still a downcycling process. A pre-separation process is one of many very important steps to obtain high-value-added products after a chemical treatment process to fulfil the requirements of the circular economy.

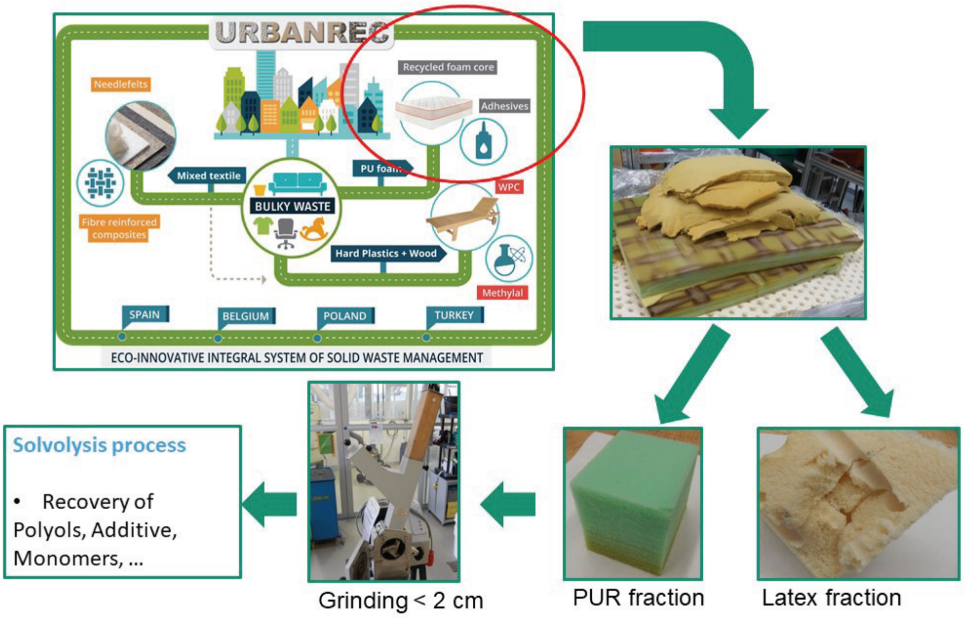

Figure 1: Objectives of Fraunhofer ICT

2 Materials and Methods

2.1 Materials

Table 1: Used materials

Chemicals	Company
Post-consumer foam material	Ecofrag
Diethylene glycol, tech. 98 %	Carl Roth
Several Catalyst	
PEP	BASF

2.2 Methods

2.2.1 Spectroscopic methods

The Raman spectroscopy was performed with a Bruker RFS 100 raman spectrometer (Nd:YAG, 1064 nm).

For the attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy a FTIR spectrometer Nicolet 6700 from Thermo Scientific and a DuraScope diamond ATR unit were used.

The FT-NIR spectroscopy was performed with a MATRIX-F FT-NIR spectrometer.

2.2.2 Glycolysis process

The general glycolysis experimental procedure is illustrated in Figure 2. The chemical recycling process of the foam began with grinding to the required size using a cutting mill and simultaneously determining the water content. Next, the foam is subjected to glycolysis using different glycols and a catalyst. The reactions are carried out at 200°C for 6 hours. Usually, two phases are obtained after cooling down the reaction, the top phase being polyol rich. Afterwards, several analyses are conducted.

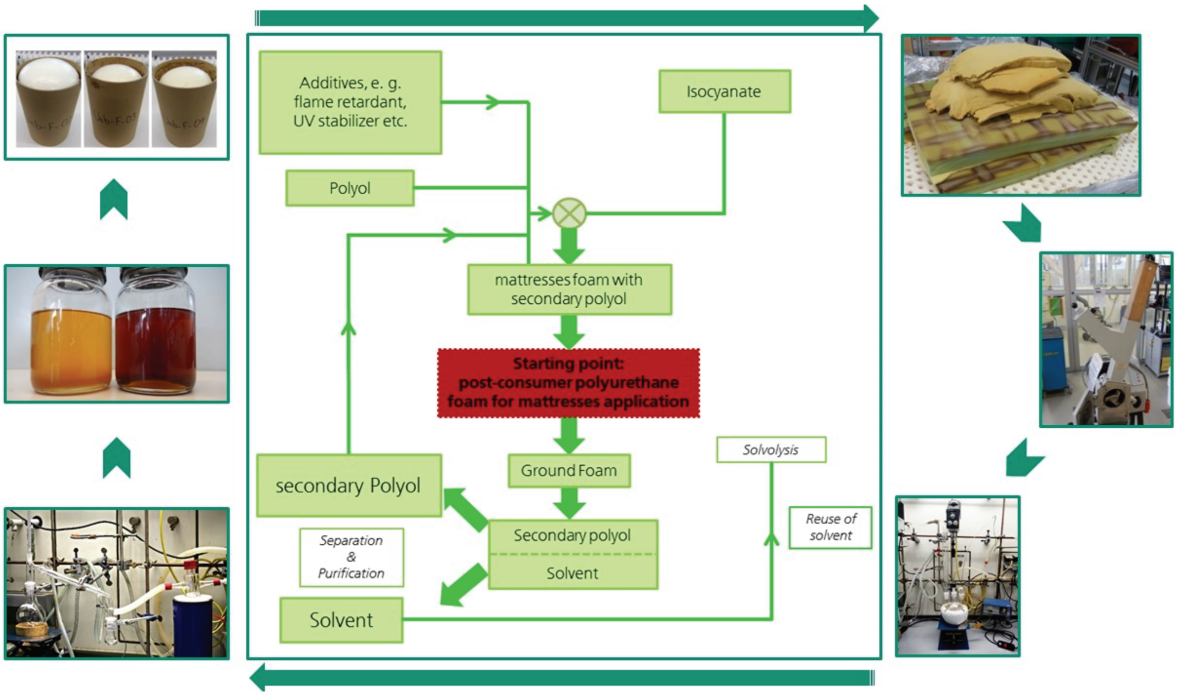

Figure 2: Chemical recycling scheme of glycolysis process

2.2.3 Foaming process

The synthesis of polyurethane foam is carried out using standard petroleum-based polyol and secondary polyol (obtained from glycolysis) in various mass ratios aided by the use of a catalyst mixture. The parameters such as height, temperature, pressure and the dielectric constant are monitored and recorded using FOAMAT Type 281 from Format Messtechnik GmbH. The data recording starts with the 10 s stirring step after isocyanate is added to the polyol mixture. This premixture is then transferred immediately onto the cardboard cylinder (radius: 75 mm, height: 230 mm), where the foaming occurred and all measurements were performed.

3 Discussion

3.1 Spectroscopic analysis

Mixed bulky waste contains hard plastic, wood, textiles and polyurethane materials from mattresses. The composition is around 80 % polyurethane materials and 20 % latex materials. Due to their chemical structure, latex materials are incinerated. Polyurethane material can be chemically recycled through solvolytic processes e.g. acidolysis and glycolysis. Impurities such as metals, latex, wood or textiles interfere with the solvolytic process. Another aspect is the different composition of polyurethane materials such as ether, ester, TDI and MDI.

Figure 3: Foam separation coming from bulky waste, ©Rampf Eco Solutions

Raman spectroscopy can be used to distinguish isocyanate TDI and MDI, whereas FTIR spectroscopy can easily distinguish ether and ester materials. The drawbacks of these methods are that they cannot be used for fast detection in industrial processes due to the long detection time and safety aspects. For this reason, NIR spectroscopy on different polyurethane materials was investigated within the Urbanrec project in collaboration with Rampf and Metrohm.

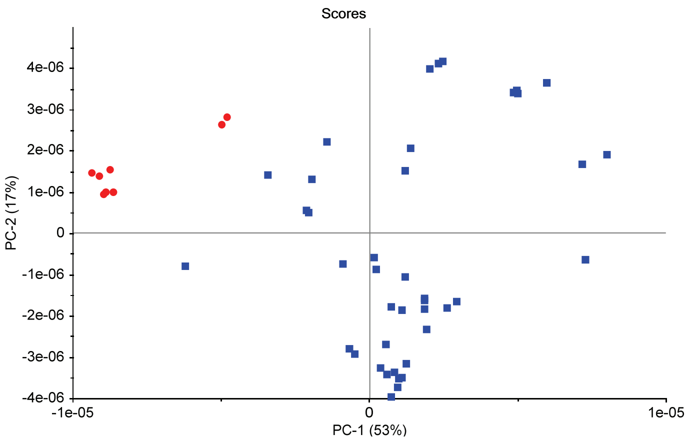

Figure 4: PC Analysis applied for distinction of polyether (blue) and polyester (red) based polyurethane material

Figure 4 shows the PC analysis which was applied to distinguish between polyether and polyester materials. It can be concluded that the clustering was successful, but that more data are necessary to confirm the model.

Figure 5 shows the PC analysis which was applied to distinguish between materials based on the isocyanates TDI and MDI. This quick analysis showed that the distinction is possible. The combination of the results is illustrated in Figure 6: polyurethane materials can be distinguished according to the four most frequently used materials.

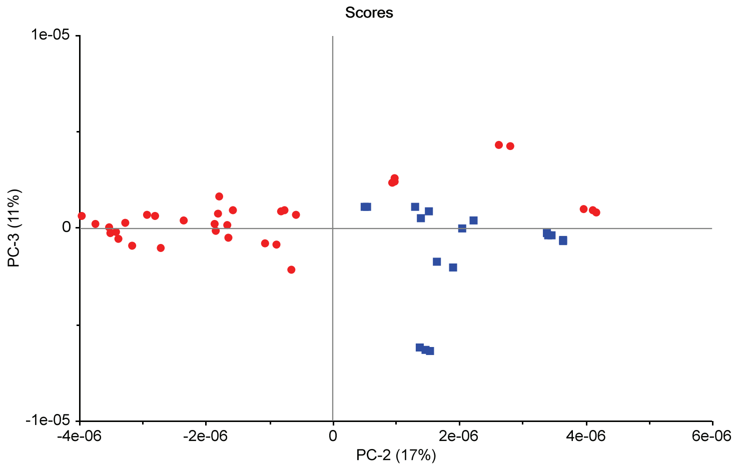

Figure 5: PC analysis applied for distinction of MDI (red)- and TDI (blue)-based polyurethane material

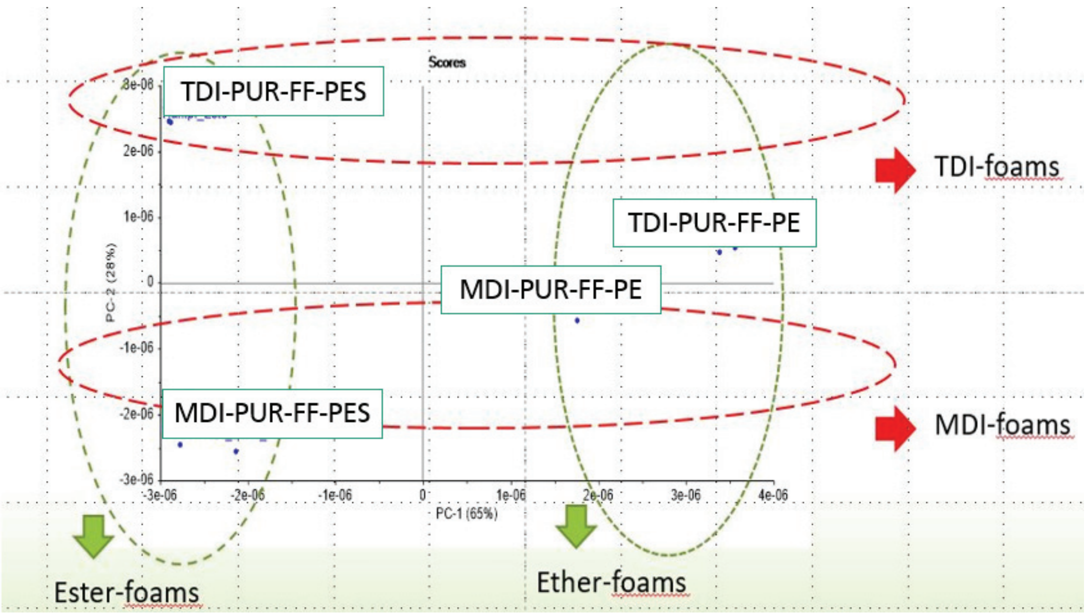

Figure 6: PC analysis for distinction of different polyurethane materials according to polyol and isocyanate component

3.2 Recovery polyol analysis

Fehler! Ungültiger Eigenverweis auf Textmarke. provides an overview of the glycolysis trials. The aim is a high recovery rate of the polyol, measured via the OH number (40 – 60 mgKOH/g), and a low concentration of TDA due to its toxicity. The concentration of TDA should be lower than 0.1 mg/ml.

Table 2: Analysis of recovered polyol from glycolysis trials

Trial	Glycol	OH-number [mgKOH/g]	Concentration of TDA [mg/mL]
Urb-G-012	DEG	60.0 ± 0.6	0.6887
Urb-G-014	PEP	66.3 ± 15.5	0.3996
Urb-G-015	PEP	68.0 ± 9.4	0.9032
Urb-G-016	DEG	101.1 ± 0.9	1.4525
Urb-G-017	DEG	101.8 ± 0.1	-
Urb-G-018	DEG	109.9 ± 3.2	2.0115
Urb-G-019	DEG	140.3 ± 1.4	-
Urb-G-020	DEG	143.9 ± 1.4	1.9701
Urb-G-021	DEG	143.0 ± 0.5	-
Urb-G-022	PEP	59.2 ± 3.4	1.0899
Urb-G-024	PEP	61.4 ± 2.2	0.9078
Urb-G-026	PEP	70.8 ± 1.6	1.5521
Urb-G-027	PEP	55.5 ± 0.7	0.2889
Urb-G-028	PEP	65.1 ± 1.0	1.074
Urb-G-029	PEP	51.1 ± 0.5	0.3502
Urb-G-030	PEP	46.5 ± 0.7	0.4602
Urb-G-032	PEP	110.2 ± 1.3	3.5656
Urb-G-033	PEP	55.6 ± 1.4	0.7139
Urb-G-034	DEG	93.4 ± 1.5	4.2954
Urb-G-037	DEG	115.3 ± 8.6	-
Urb-G-038	DEG	97.7 ± 13.5	0.7008
Urb-G-039	PEP	21.5 ± 0.1	0.0662
Urb-G-040	DEG	89.60 ± 1.2	1.1116
Urb-G-041	DEG	76.3 ± 2.3	0.9132
Urb-G-042	DEG	95.5 ± 20.8	1.1096
Urb-G-043	DEG	95.2 ± 8.7	0.7239
Urb-G-044	DEG	87.8 ± 1.1	0.7070
Urb-G-045-L	DEG	94.1 ± 0.2	0.2112
Urb-G-045-S	DEG	221.5 ± 12.7	0.6638
Urb-G-046	DEG	81.5 ± 13.6	1.0683

3.3 Foam analysis with recovered polyol

Figure 7 shows the rise profile of the manufactured foam. The incorporation of 30 pphp secondary polyol only produces a small difference in the rise height of the foam. Urb-F-06 show a lower reactivity due to delayed start of rising, and after approximately 180 s the foams collapse and shrink.

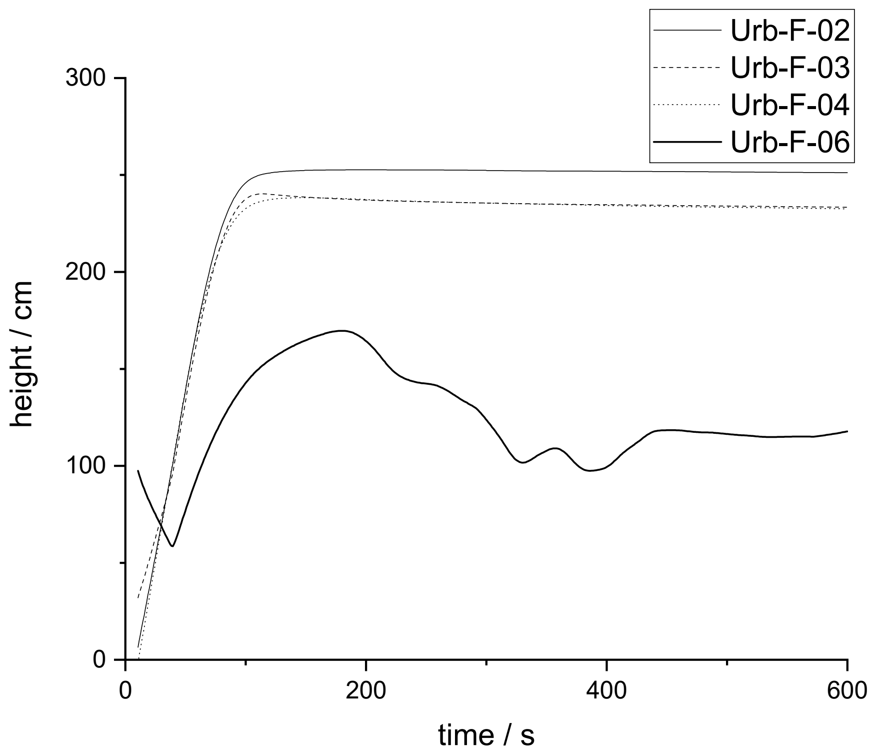

Figure 7: Foaming profile of manufactured foams

Table 3 illustrated the foam trials with secondary polyol. The mass ratio of polyol to isocyanates remains constant.

Table 3: Foaming test with secondary polyol.

Trial	PEP [g]	Secondary Polyol [g]	Water-Additive Mixture [g]	TDI 80/20 [g]
Urb-F-01	100	0	5.163	50.30
Urb-F-02	90	10	5.163	50.48
Urb-F-03	80	20	5.163	50.66
Urb-F-04	70	30	5.163	50.84
Urb-F-05*	50	50	5.163	51.20
Urb-F-06*	100	0	5.163	50.30

* foam collapse

Figure 8 shows the manufactured foam. As also visible in Figure 7, the rising heights of the different materials are almost equal. The mechanical value such as density and air permeability in Table 4 are also almost identical.

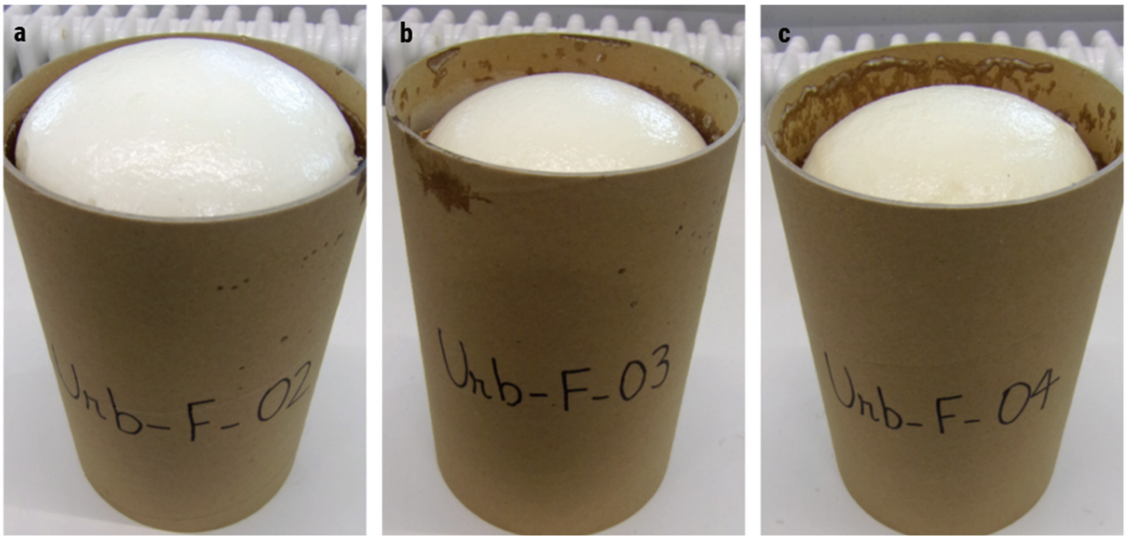

Figure 8: PU foams obtained using various ratios of secondary polyol (a) 10 phpp, (b) 20 phpp and (c) 30 phpp

Table 4: Mechanical properties of TDI-foams

Trial	Density [kg/m^3]		Average Air Permeability [dm^3/s]	Standard Variance
Standard TDI Foam	31.25	Top	0.128	0.011
		Bottom	0.312	0.006
Urb-F-02	28.26	Top	0.085	0.008
		Bottom	0.055	0.003
Urb-F-03	29.92	Top	0.159	0.014
		Bottom	0.091	0.005
Urb-F-04	25.94	Top	0.135	0.016
		Bottom	0.043	0.009

3.4 Conclusion and further investigations

The differentiation of chemically different polyurethane systems could be demonstrated by Raman, FTIR-ATR and NIR spectroscopy. This paves the way for a suitable separation process before solvolysis to obtain a high-quality recycled product.

Within the Urbanrec Project, Fraunhofer ICT shows that 30 pphp secondary polyol obtained from solvolysis can be incorporated into a flexible foam formulation. Further mechanical testing such as tensile strength, resilience, hardness etc. would be necessary to validate the quality of the foam materials.

Currently ongoing research projects focus on the recycling economy [4, 5, 6]. The investigation of a design-for-recycling approach and new tailor-made chemical recycling process is necessary to fill the gap and achieve a circular economy.

4 Literature

[1] D. Simòn, A. M. Borreguero, A. de Lucas, J. F. Rodríguez, Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability, *Waste Management*, Vol. 76, pp. 147-171, 2018.

[2] M. Baumgartner, A. Duvielguerbigny, PU Europe, The end of life of flexible and rigid polyurethane foam: EU Regulatory update and way forward for the industry, **UTECH 2018**.

[3] M. Moeller, Addressing Challenges and Opportunities of the Circular Economy, **UTECH 2018**.

[4] https://www.livingcircular.veolia.com/en/inspirations/partnered-veolia-eco-mobilier-recycling-our-old-pillows, accessed on 24.01.2019, 18:26.

[5] https://www.kunststoffweb.de/ki_ticker/DowDuPont_Chemisches_Recycling_von_PUR_mit_H_S_t238357, accessed on 21.01.2019, 17:50.

[6] Covestro, Improving the recycling of polyurethane plastics, https://press.covestro.com/news.nsf/id/Improving-therecycling-of-polyurethane-plastics, press release, accessed on 29.01.2019.