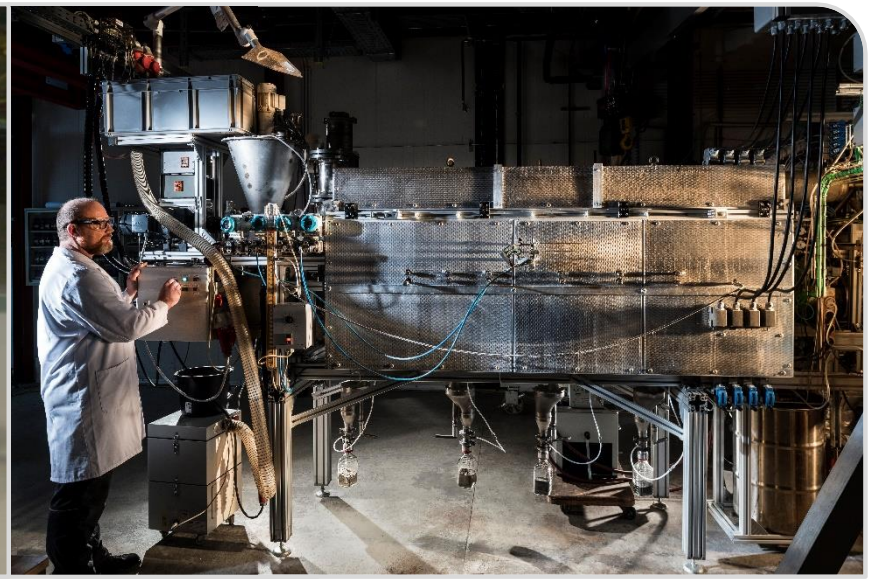
Karlsruher Institut für Technologie

Institut für Technische Chemie

Thermogravimetric studies and kinetic modeling of the pyrolysis of polyurethane plastics

Michael Zeller, Tilman Saatzer, Daniela Merz, Dieter Stapf

PYRO Ghent 05/2022

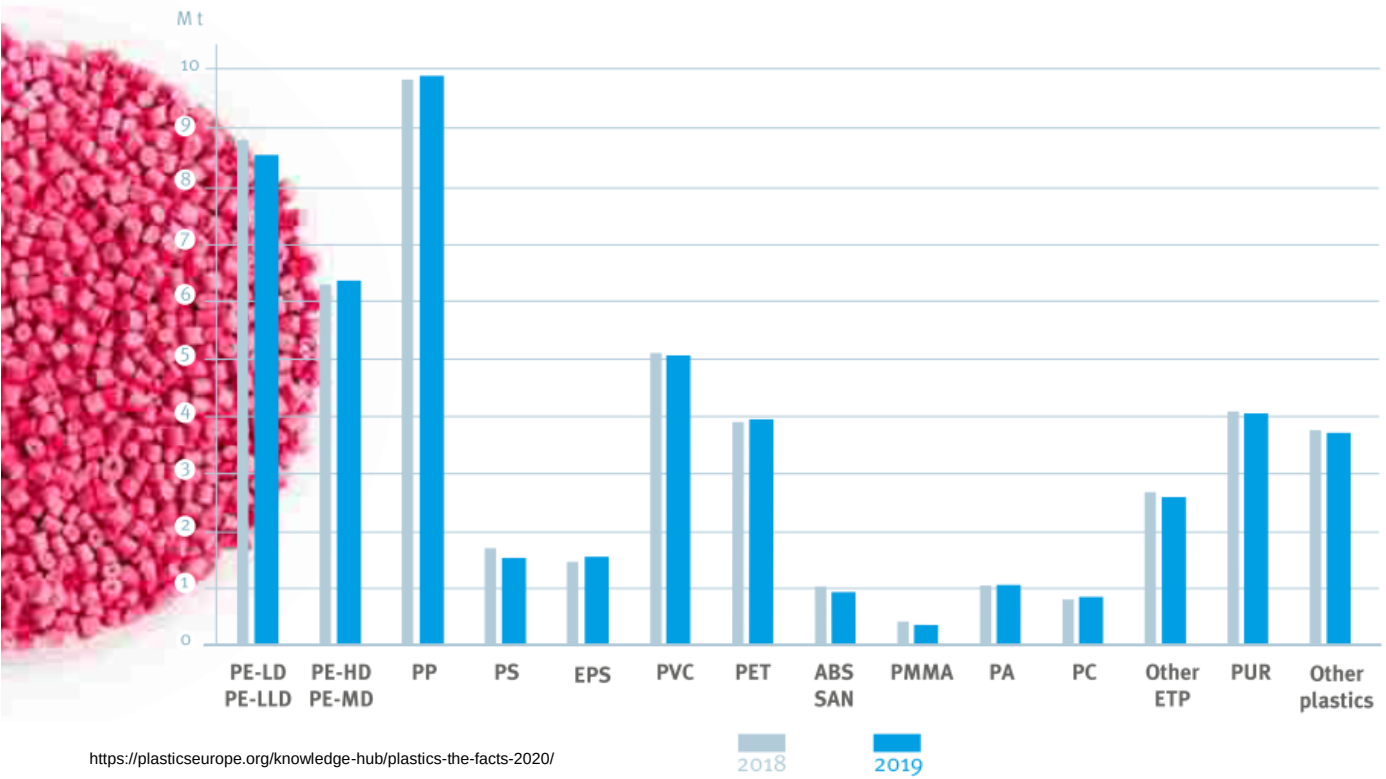


Introduction

SOURCE: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH

PLASTICS DEMAND BY RESIN TYPE 2019

Distribution of European (EU28+NO/CH) plastics converters demand by resin type in 2019.
Leading polymers are the polyolefins (PE & PP).



https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/

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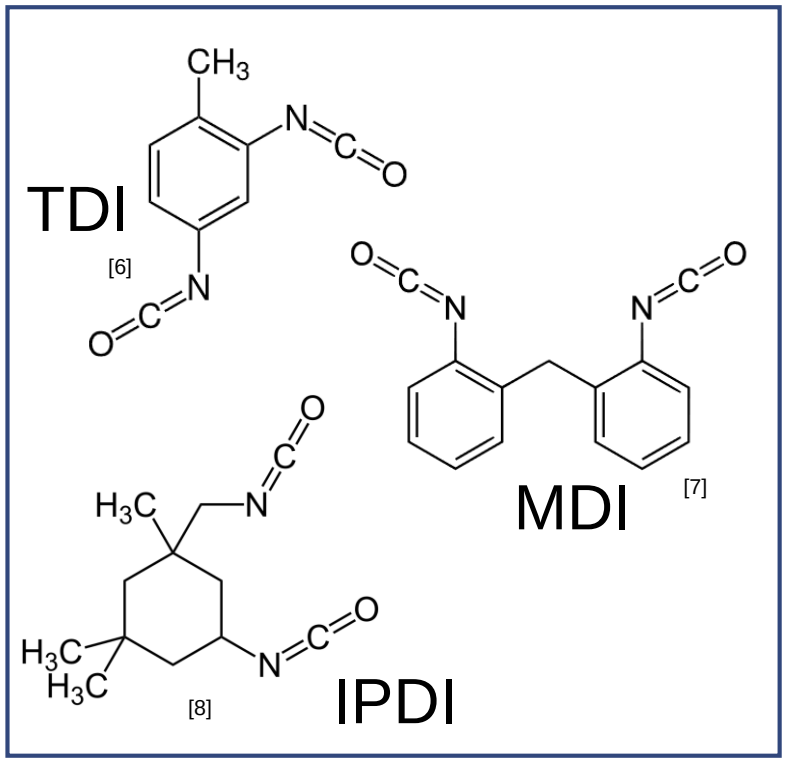
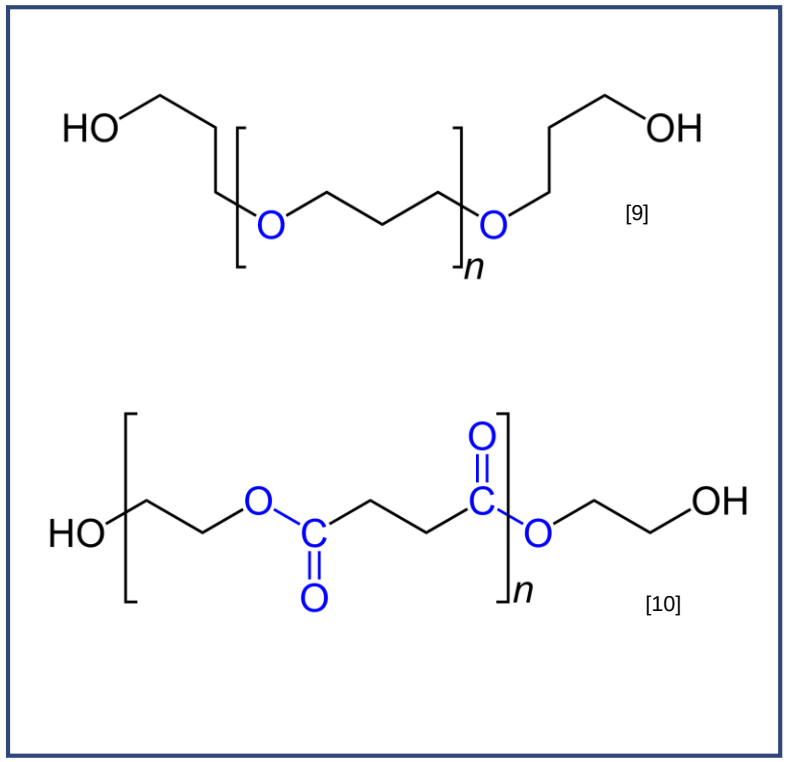
Polyurethane Chemistry

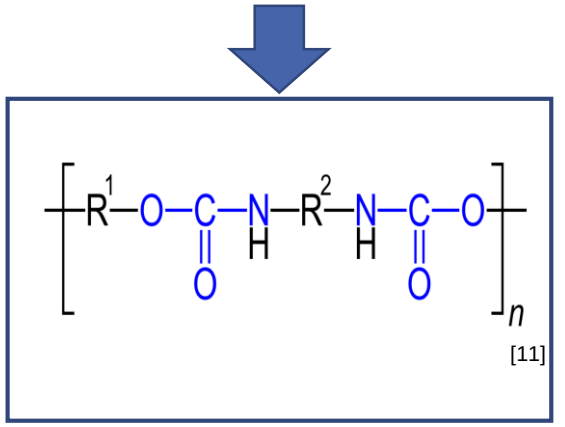


Isocyanates



Polyols

- Foaming agents
- Cross Linkers
- Flame Retardants
- Stabilizers
- Fillers …



Polyurethanes

[6] Von Chem Sim 2001 - Eigenes Werk, Gemeinfrei, https://commons.wikimedia.org/w/index.php?curid=78819735

[7] Von Yikrazuul - Eigenes Werk, Gemeinfrei, https://commons.wikimedia.org/w/index.php?curid=5046205

[8] Von Jü - Eigenes Werk, Gemeinfrei, https://commons.wikimedia.org/w/index.php?curid=81399249

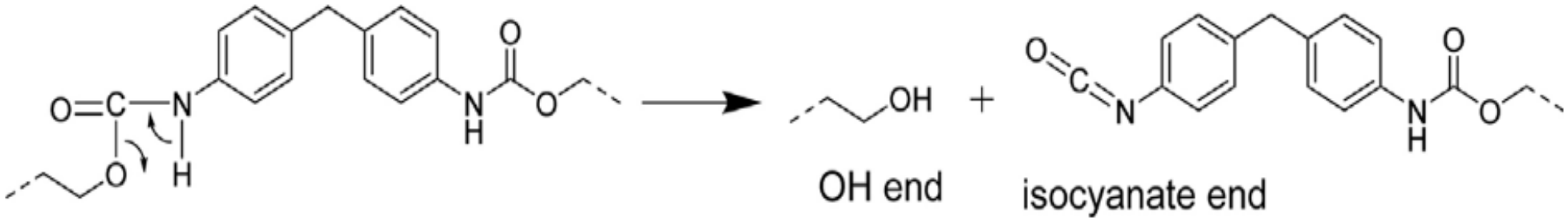
[9] Von Jü - Eigenes Werk, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=36661045

[10] Von Jü - Eigenes Werk, Gemeinfrei, https://commons.wikimedia.org/w/index.php?curid=42160752

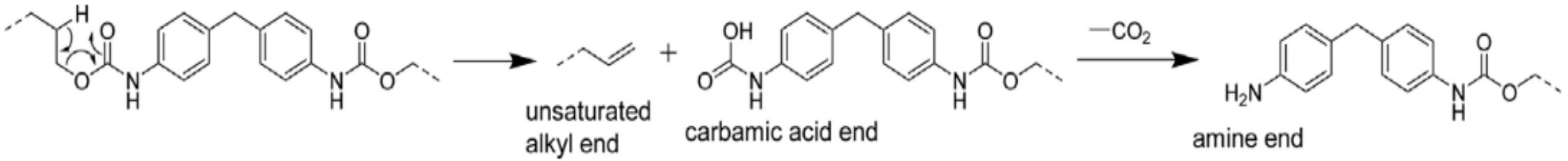
[11] Von Roland.chem - Eigenes Werk, CC0, https://commons.wikimedia.org/w/index.php?curid=36670935

Characteristics of Polyurethane Degradation

a



b



Kumagai, Shogo; Motokucho, Suguru; Yabuki, Ryosuke; Anzai, Airi; Kameda, Tomohito; Watanabe, Atsushi et al. (2017): Effects of hard- and soft-segment composition on pyrolysis characteristics of MDI, BD, and PTMG-based polyurethane elastomers. In: *Journal of Analytical and Applied Pyrolysis* 126, S. 337–345. DOI: 10.1016/j.jaap.2017.05.012.

Material Selection - Model Polyurethanes

Flexible Foam

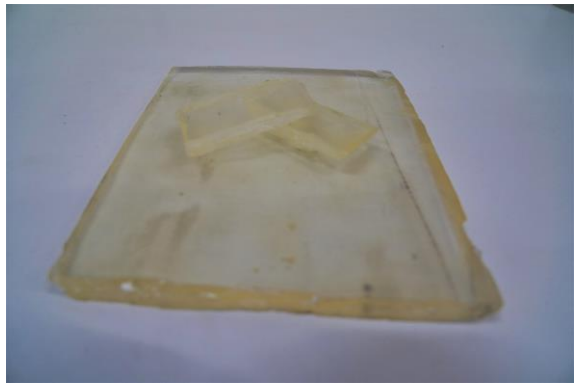
Rigid Foam

MDI/PMDI + EO&PO-Polyether-ols

Foaming agent: Water

Thermoplastic PUR

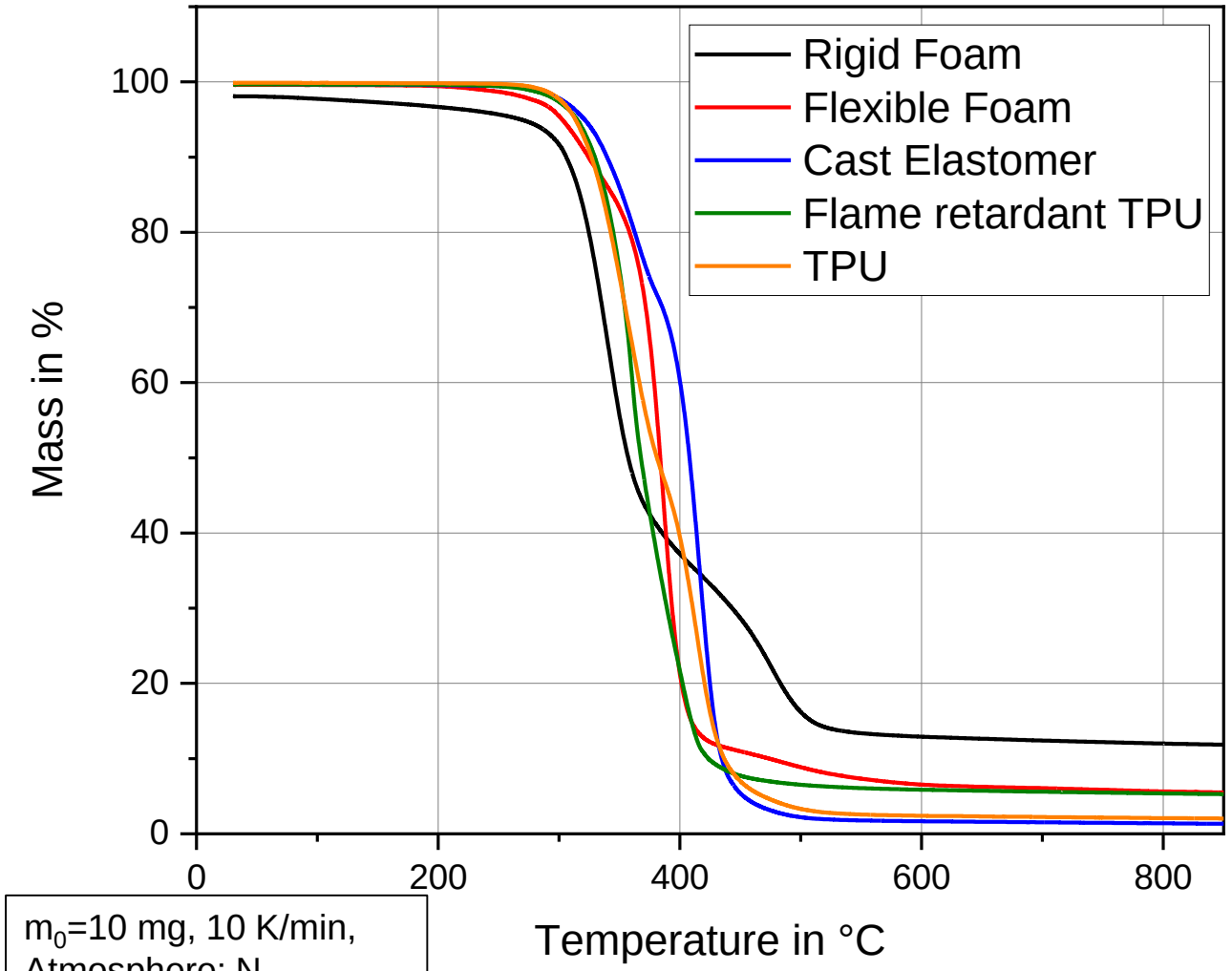
Flame Retarded TPU



Cast Elastomer

MDI + PolyTHF

Thermogravimetry – Kinetic Modeling



m_0=10 mg, 10 K/min,
Atmosphere: N_2

$$w_{cal} = 1 - \alpha_1 v_{1\infty} - \alpha_2 v_{2\infty}$$

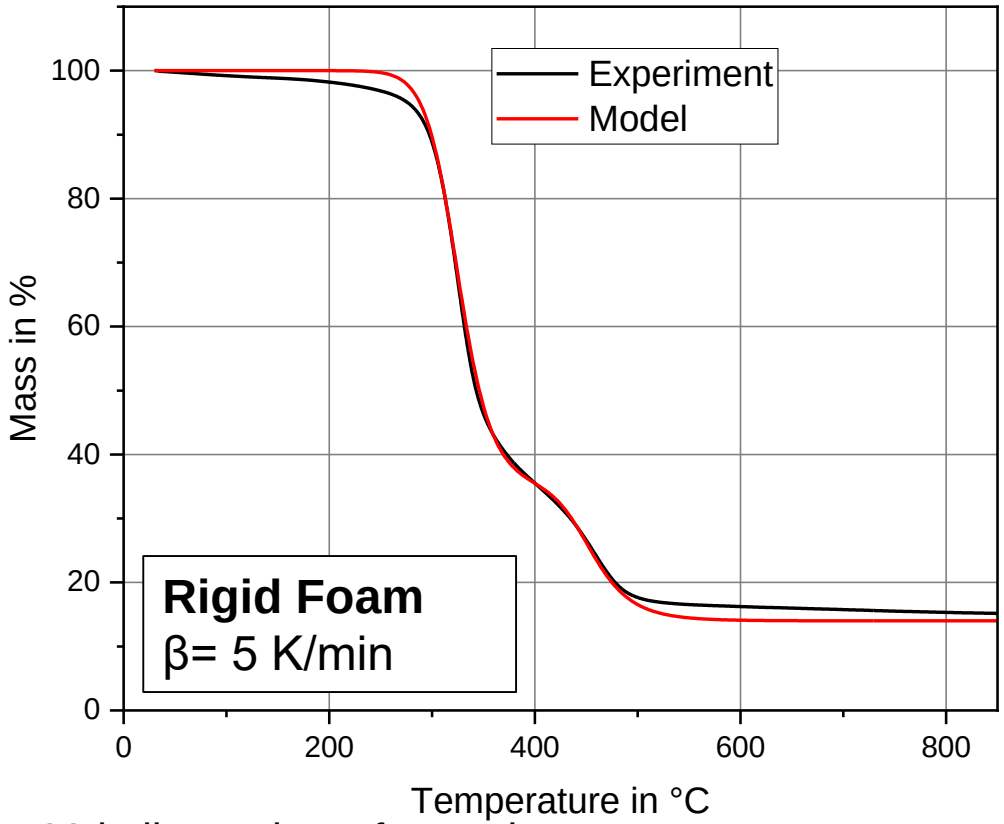
$$\frac{d(v_1/v_{1\infty})}{dT} = \frac{d\alpha_1}{dT} = \frac{k_{0,1}}{\beta} exp\left(\frac{-E_{A,1}}{RT}\right)(1-\alpha_1)^{n_1}$$

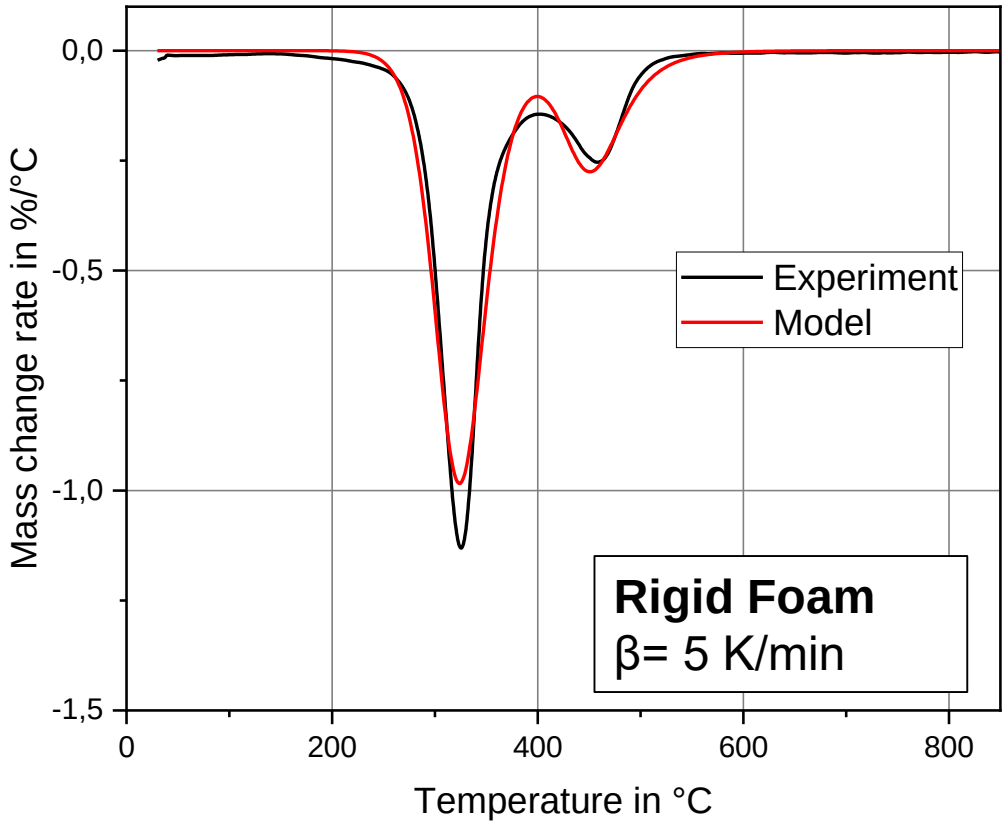
$$\frac{d(v_2/v_{2\infty})}{dT} = \frac{d\alpha_2}{dT} = \frac{k_{0,2}}{\beta} exp\left(\frac{-E_{A,2}}{RT}\right)(\alpha_1-\alpha_2)^{n_2}$$

Fit Parameters

from Garrido et al. 2016 (https://doi.org/10.1016/j.enconman.2016.04.048)

Kinetic Modeling – work in progress





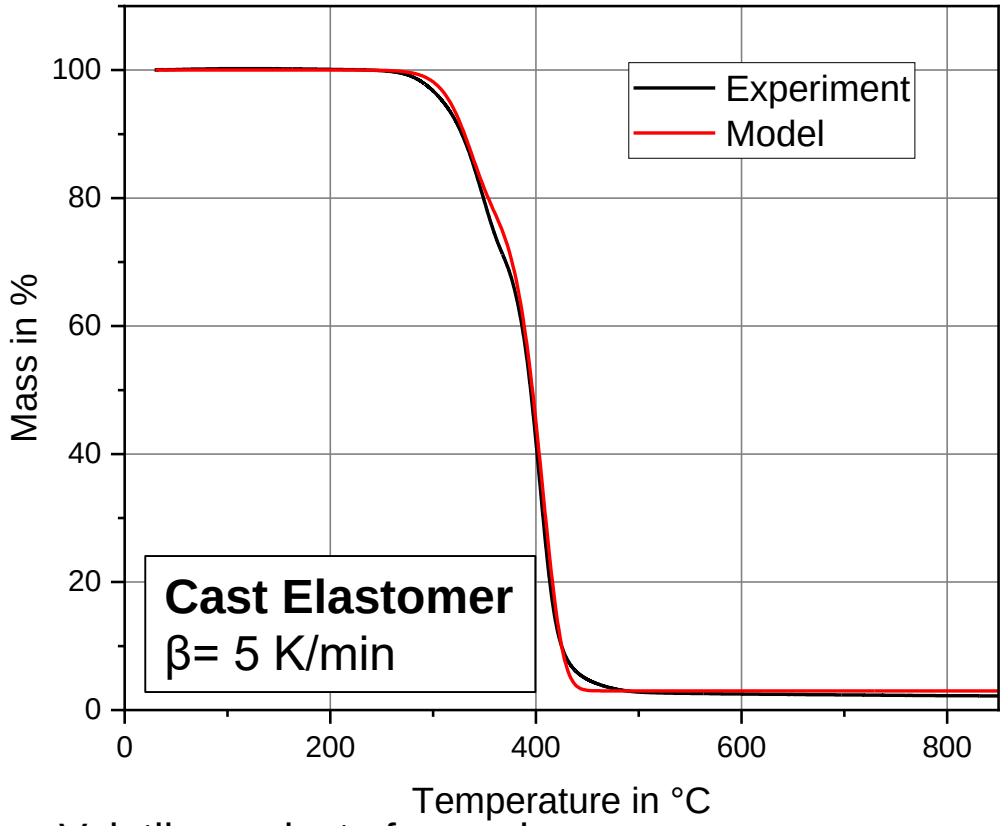
Exp. Volatile products from primary degradation:

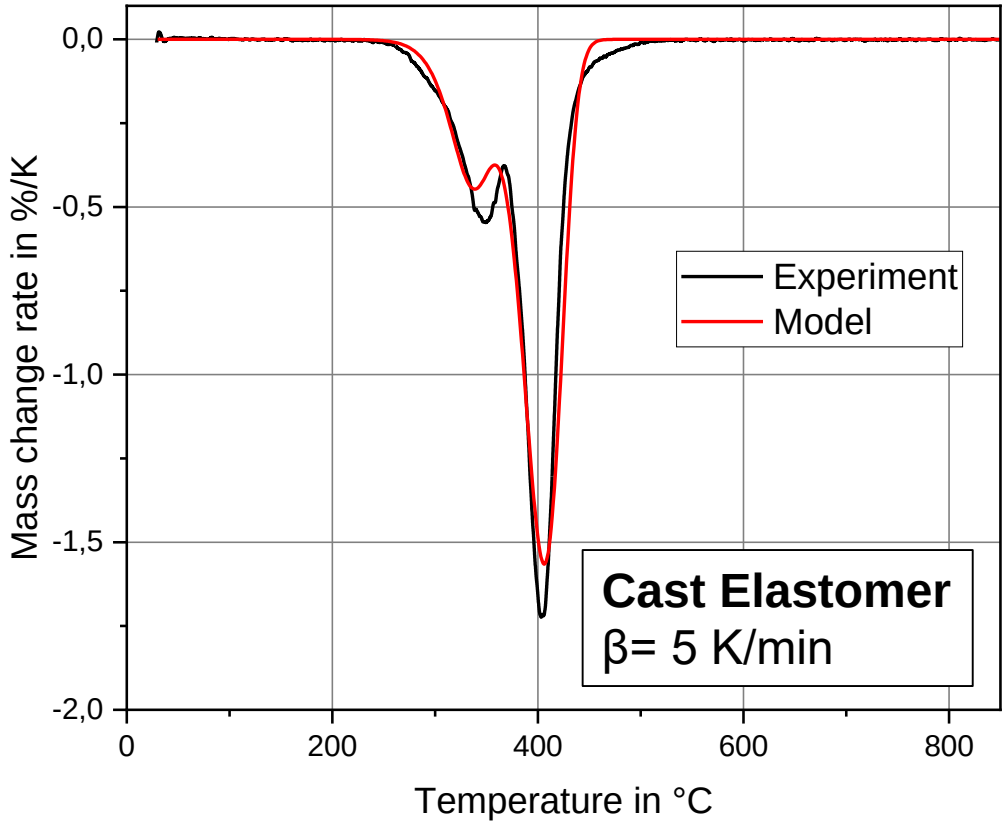
- MDI (56 wt.% in PUR)
- Glycerine (4 wt.% in PUR)
- Sorbitol (7 wt.% in PUR)

$\approx \nu_{1\infty}$

$\nu_{1\infty}$	$\nu_{2\infty}$	$E_{A,1}$	$E_{A,2}$	$k_{0,1}$	$k_{0,2}$	n_1	n_2
-	-	kJ/mol	kJ/mol	1/s	1/s	-	-
0,65	0,21	175	238	$9{,}37*10^{12}$	$6{,}41*10^{14}$	2,05	2,37

Kinetic Modeling – work in progress





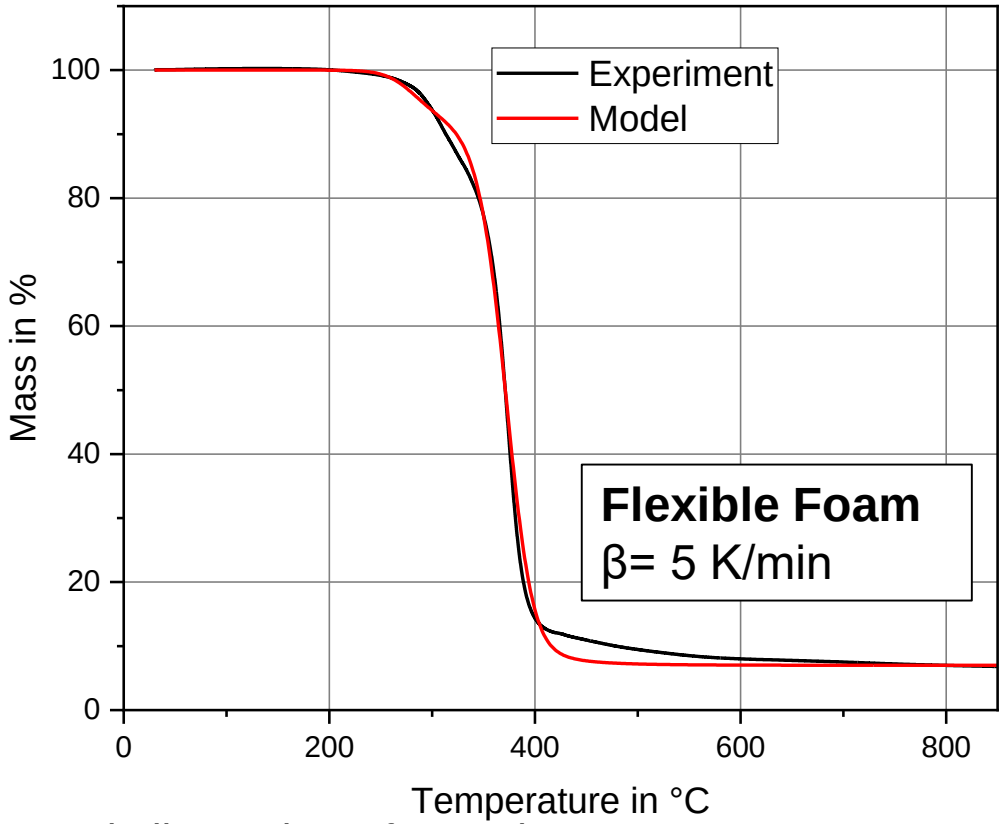
Exp. Volatile products from primary degradation:

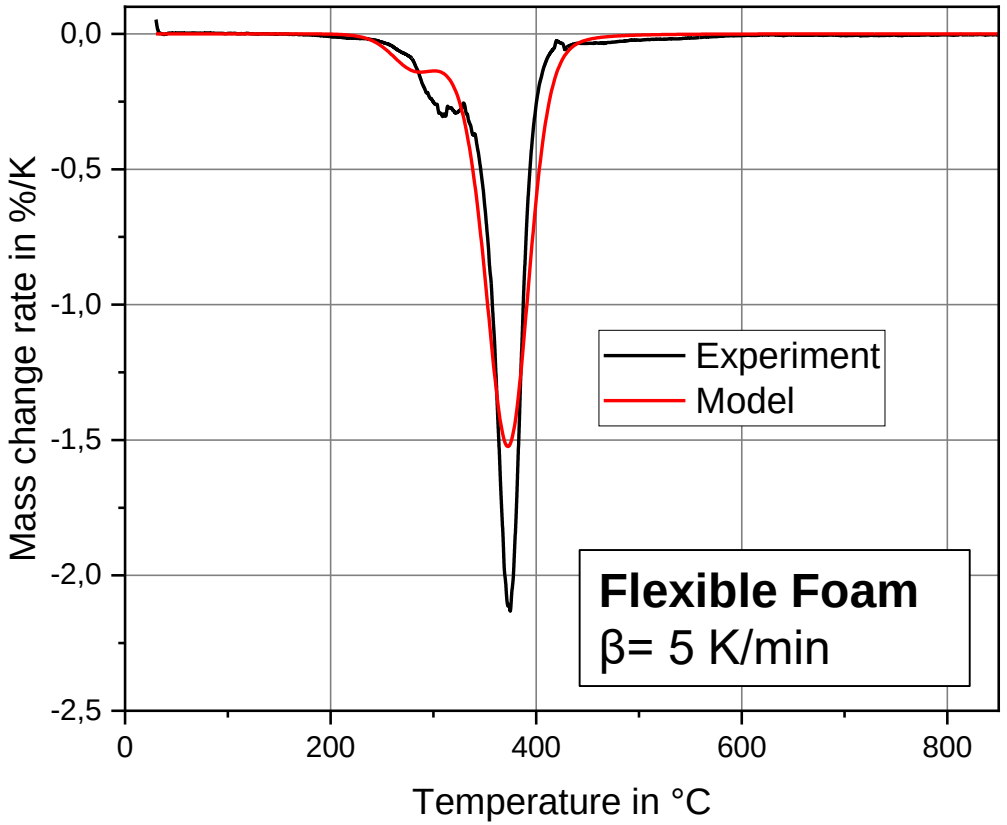
- MDI (20 wt.% in PUR)
- 1,4-BDO (2 wt.% in PUR)

$\approx \nu_{1\infty}$

$\nu_{1\infty}$	$\nu_{2\infty}$	$E_{A,1}$	$E_{A,2}$	$k_{0,1}$	$k_{0,2}$	n_1	n_2
-	-	kJ/mol	kJ/mol	1/s	1/s	-	-
0,21	0,76	178	223	$9{,}23*10^{12}$	$6{,}24*10^{14}$	1,22	1,16

Kinetic Modeling – work in progress





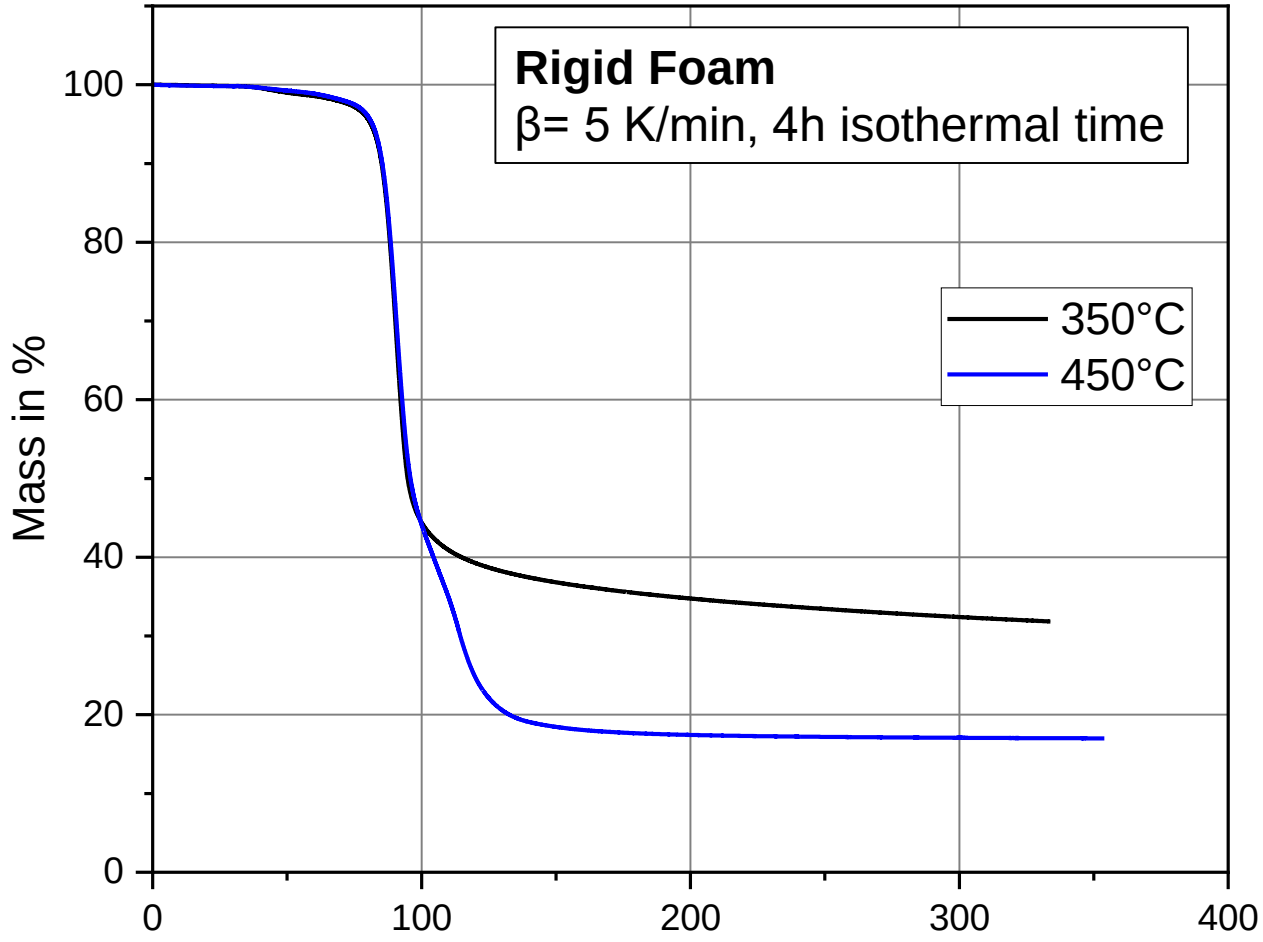
Exp. Volatile products from primary degradation:

- MDI (29 wt.% in PUR)
- Glycerine (2 wt.% in PUR)

$\neq \nu_{1\infty}$

$\nu_{1\infty}$	$\nu_{2\infty}$	$E_{A,1}$	$E_{A,2}$	$k_{0,1}$	$k_{0,2}$	n_1	n_2
-	-	kJ/mol	kJ/mol	1/s	1/s	-	-
0,10	0,83	171	203	$4{,}92*10^{13}$	$1{,}26*10^{14}$	2,86	1,50

Preperative TGA – work in progress



Residual mass @ 900°C = 15,6%

- Slow isothermal mass loss
  - → slow degradation reactions
  - → little volatiles generation
  - → N-Release?

T	Element Balance		
°C	% Feedstock **C**	% Feedstock **H**	% Feedstock **N**
350	37	27	55
450	19	9	25

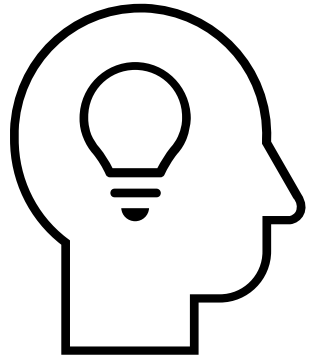
→ TG-FTIR, Py-GC-MS

Conclusions & Outlook

- Two-step mechanism confirmed for broad range of PURs ✓
- Kinetic Model can reproduce overall mass loss and peak temperatures well ✓

Current & Future work

- Expansion of model dataset with isothermal experiments
- Product evolution
  - TG-FTIR
  - Py-GC-MS → higher heating rates



- Influence of secondary reactions in lab scale pyrolysis

Image Sources

- [1] https://www.effizienzhaus-online.de/polyurethan-pur (accessed 30.4.21)
- [2] https://galusaustralis.com/2019/11/53556/polyurethane-shoe-sole-market-rising-trends-demands-and-growing-business-opportunities-2019/ (accessed 30.4.21)
- [3] https://www.caparol.de/produkte/bautenlacke-lasuren/capalac-aqua/weiss-und-buntlacke/capalac-aqua-2k-pu-lack (accessed 30.4.21)
- [4] https://www.bm-online.de/wissen/bauelemente/pu-schaum-so-gehts/ (accessed 30.4.21)
- [5] https://huber-schaumstoffe.de/index.php/pur-schaum/ (accessed 30.4.21)