Methoden und Modelle zur Lebensdauervorhersage von Thermoplasten

Experimental Techniques and Models for Service Life Prediction of Thermoplastic Polymers

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Vielen Dank an:
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Bereich Kunststoffe

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https://www.lbf.fraunhofer.de/en/laboratory-equipment/polymer-characterisation/Physical-methods.html

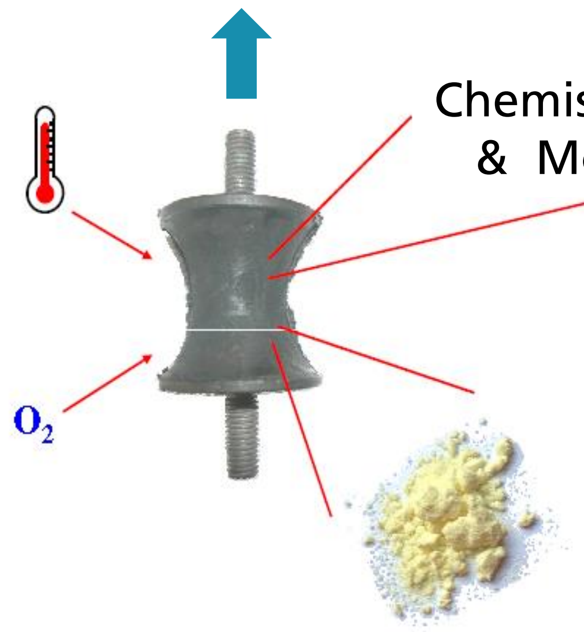
https://www.lbf.fraunhofer.de/en/laboratory-equipment/polymer-characterisation/weathering.html

Was beeinflusst die Lebensdauer?

Mechanische
Lasten

Temperatur

Chemische Struktur
& Morphologie



Additivpakete

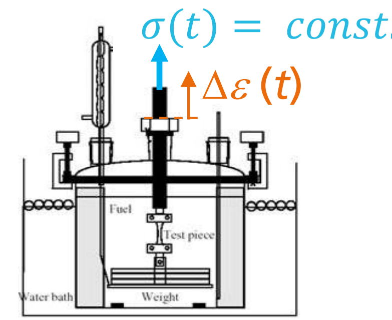
Lars Steinke, TU Hamburg-Harburg

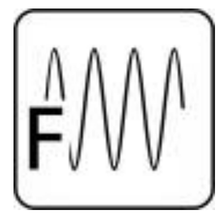
Umgebung
- Fluide
- Feuchte
- Abrasion
- …

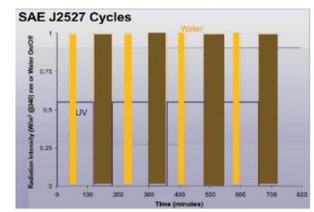
Art der Lasten

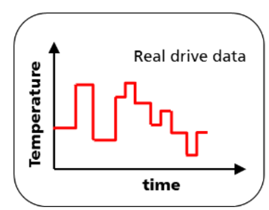
Thermisch, mechanisch, elektrisch, … Strahlung, Quellung ….

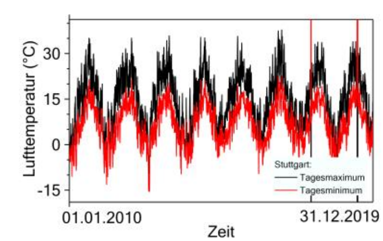
- **statisch**
  - Isotherme Ofenlagerung ($T = const.$)
  - Kriechversuche ($\sigma = const.$)
  - Spannungsrelaxation ($\varepsilon = const.$)
  - …
- **zyklisch**
  - harmonisch
  - periodisch (nicht harmonisch)
  - …
- **willkürlich**
  - Lastkollektive
  - Wetter (pseudo-arbitary)
  - pseudo-random
  - …











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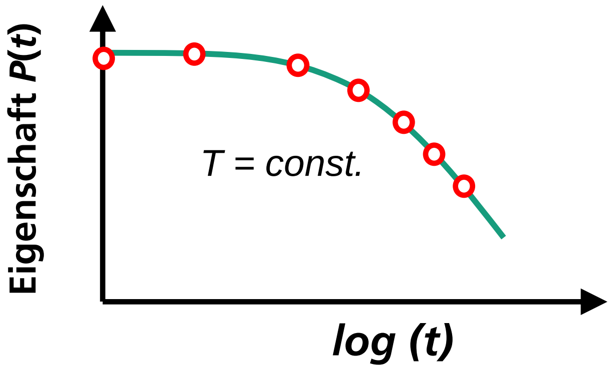
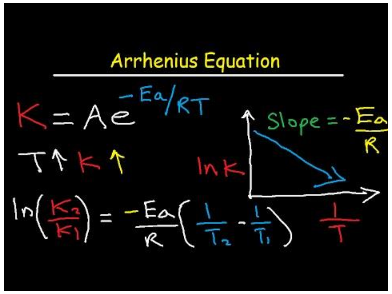
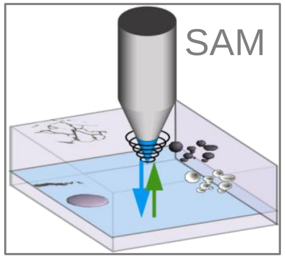
Erfassung der Lebensdauer



- **Auslagerungsversuche**
  - kontinuierliches Monitoring
  - diskontinuierliche Entnahmen



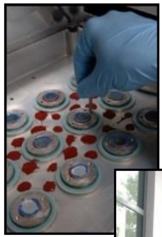
- **Beschleunigte Alterung**
  - Temperaturerhöhung (Arrhenius)
  - Dosis-Steigerung (z.B. Bestrahlungsstärke ↑)
  - Zeitraffung (z.B. keine Dunkelphase ↓)



- **Analytik, Mess- und Prüfmethoden**
  - Früherkennung von Bewitterungsschäden
  - …

Service Life Prediction @ LBF

Natural and artificial weathering



In-situ monitoring

H. Oehler

Polymer, additives, filler

↓

Processing / plastic part / coating

↓

Weathering / fatigue testing
thermal, mechanical, water, chemicals…

Testing / characterization

↓

Understanding of aging and failure mechanisms

↓

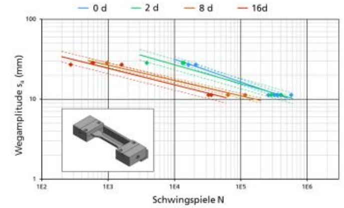
Model development
Coupling of transport equations, material and reaction models

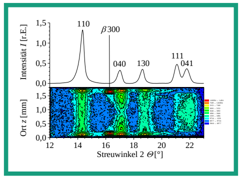
Failure criteria

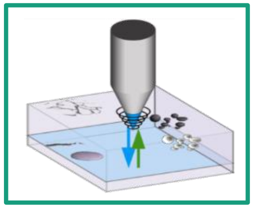
↓

Simulation (FEM…)
input data, validation

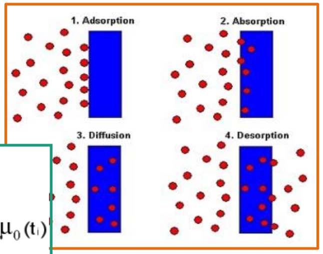
D. Lellinger J. Decker

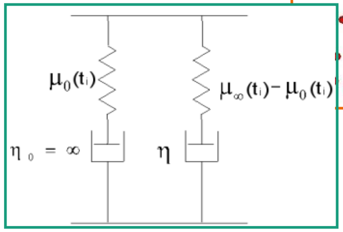




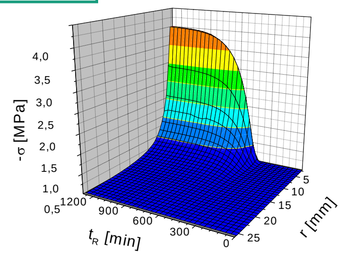


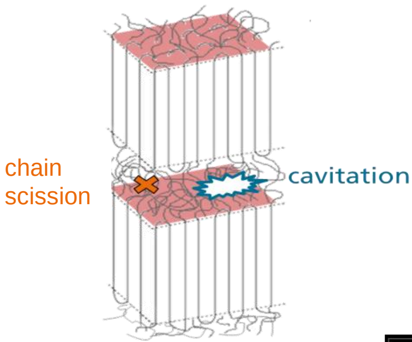
H. Oehler

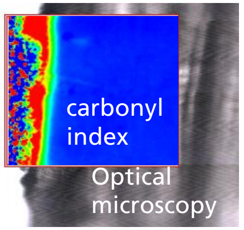




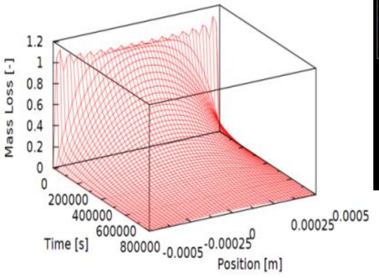
D. Lellinger
F. Dillenberger

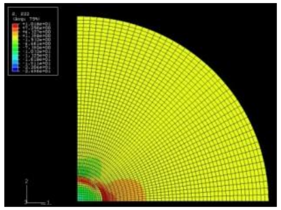






R. Brüll, B. Barton

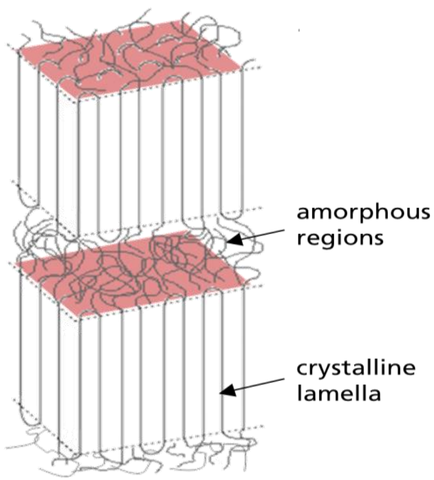


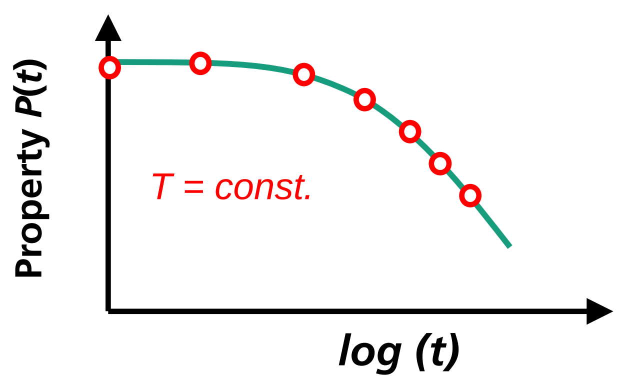


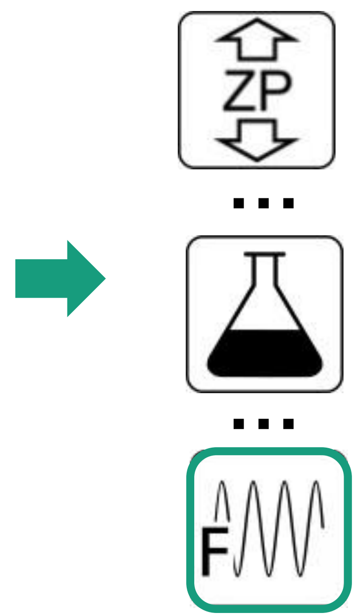
D. Lellinger
G. Geertz

Example 1
Thermal aging of semi-crystalline polymers

- Isothermal aging at different temperatures
- Properties for discrete aging times
  - including cyclic fatigue







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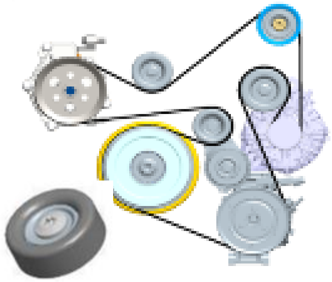
Example 1

Aging of thermoplastics in the engine compartment

Plastic parts close to the automotive engine

Engine cover



Engine pulley

HMC

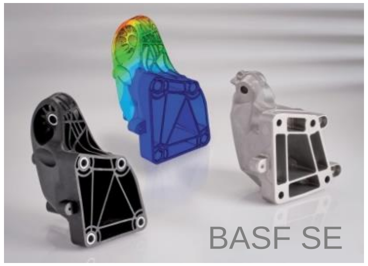
Engine compartment

Thermal load ΔT(t)

+

Outdoor exposure

Transmission cable



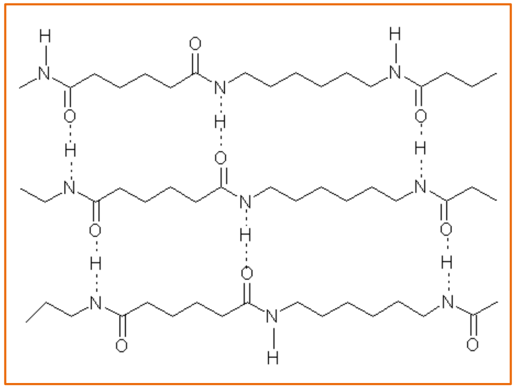
Engine support bracket

D. Lellinger, I. Alig, H. Oehler, , K. Rode, F. Malz, L.M. Herkenrath, J. Y. Youn; Accelerated thermal aging of thermoplastic materials for the motor compartment: Characterization, degradation model and lifetime prediction, in: Service Life Prediction of Polymers and Coatings, Enhanced Methods, Edited by C.C. White, M.E. Nichols, J.E. Pickett, ch. 8, Elsevier 2020, p.116 -160, (ISBN 978-0-12-818367-0).

Material and aging conditions

- Polyamide 6.6 compounds
  - containing glass fibers (GF: 50 wt. %)
  - typically additive packages

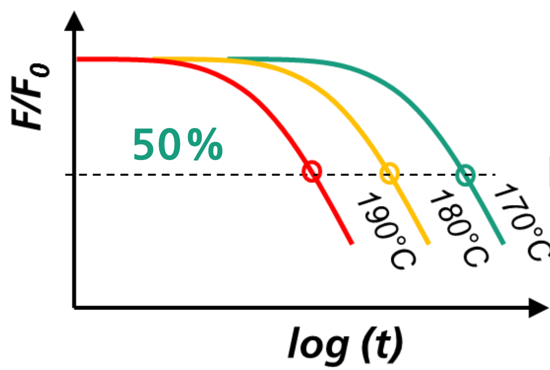
- Isothermal aging
  - pre-dried samples
  - temperatures: 140 to 220°C
  - in dry air

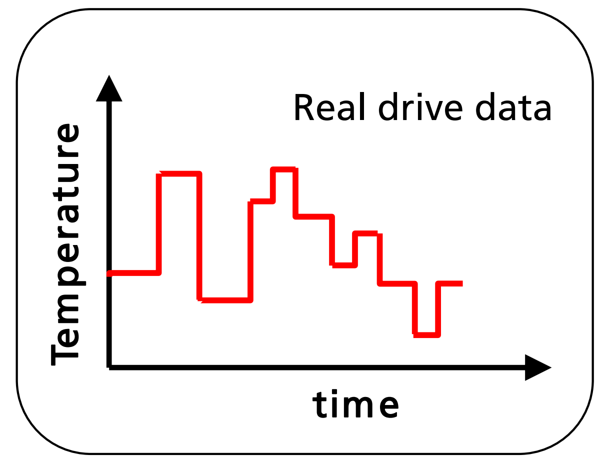


Concept
Accelerated Testing

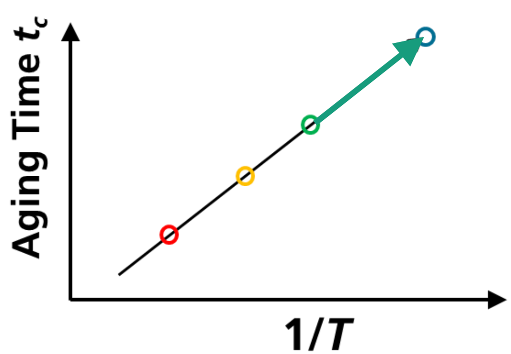
- **Characteristic time approach**

Time dependent experimental data at elevated temperatures





Arrhenius plot of characteristic times
⇒ Activation energy



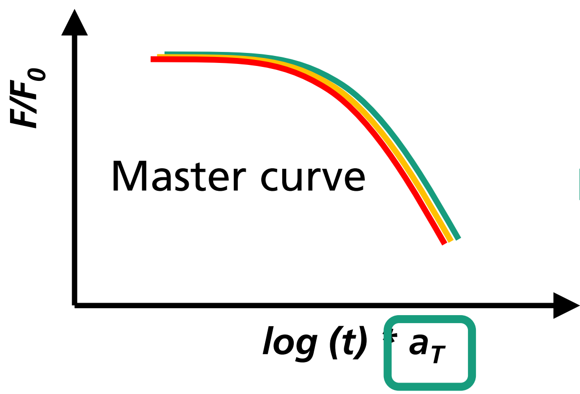
Service life prediction

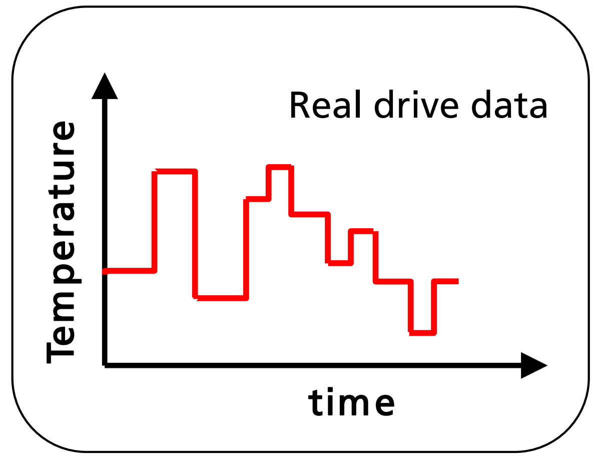
- Time to failure
- Acceleration/prolongation factors
- Equivalent aging time

Concept
Accelerated Testing

Master curve approach

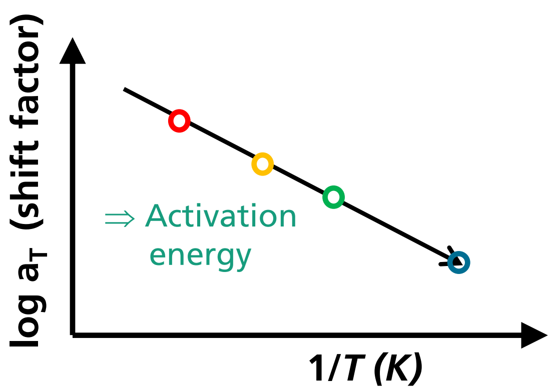
Master curve from experimental data at elevated temperatures





Arrhenius plot for shift factors

⇒ Activation energy



Service life prediction

- Time to failure
- Acceleration/prolongation factors
- Equivalent aging time

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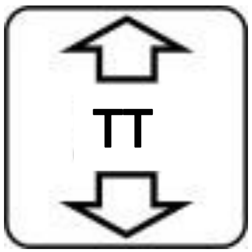
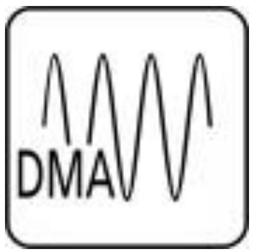
Methods

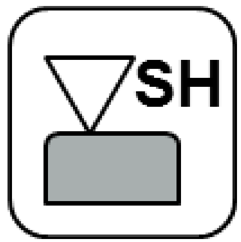
Physical and chemical characterization



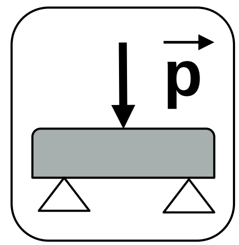
Tensile
Test

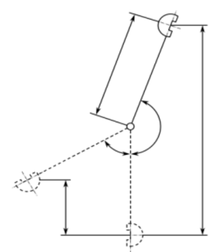


Dynamic
mechanical
analysis

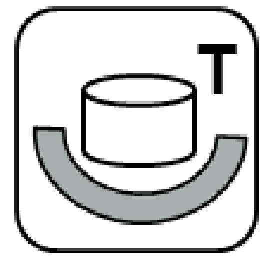


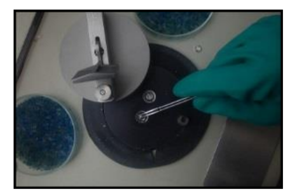
Shore
hardness





Impact
strength





Thermal
analysis
DSC, TGA
TGA-DSC

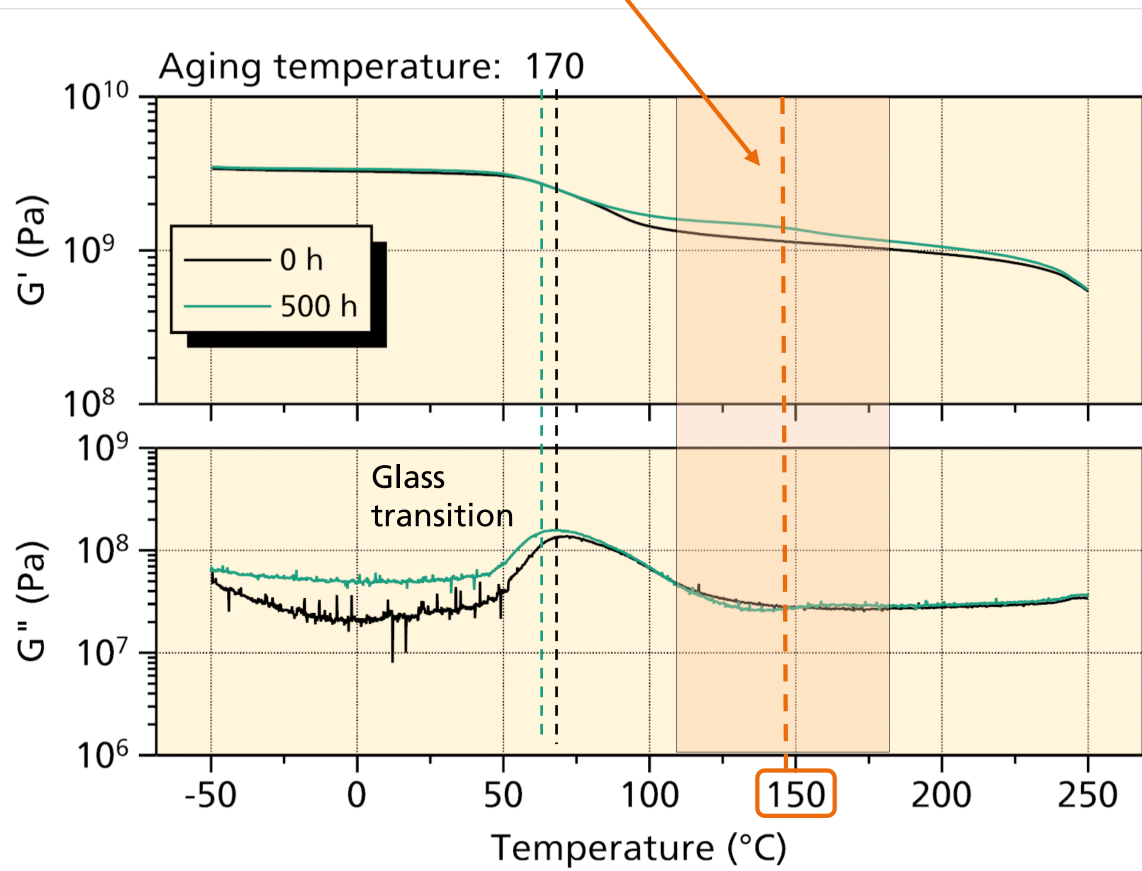
Chemical analytics
GPC, MALDI-TOF, NMR

Dynamic Mechanical Analysis

Dynamic shear modulus: G*= G'+iG''

170
[°C]

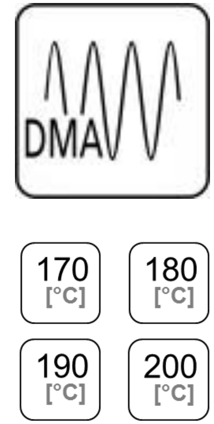
- Temperature region of engine operation



Polyamide 6.6 + GF

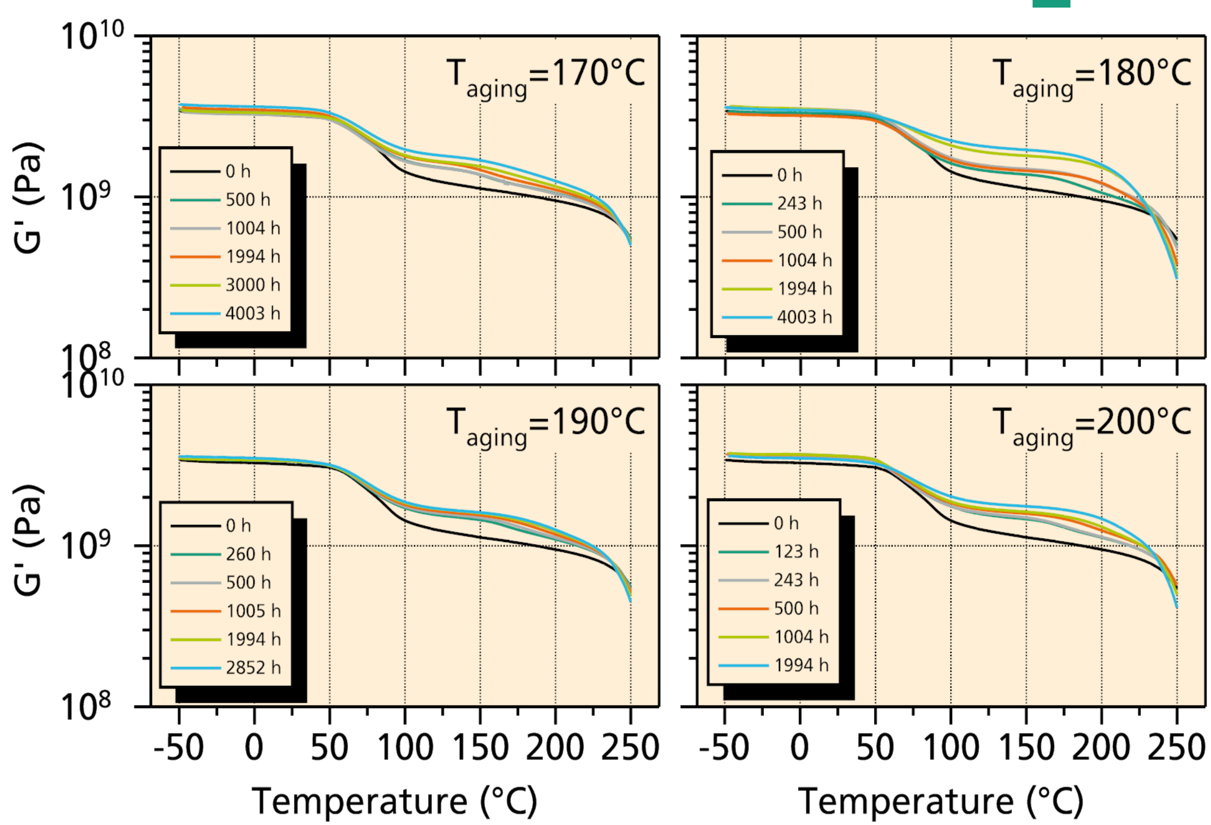
Dynamic Mechanical Analysis

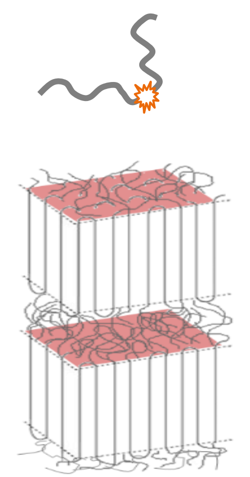
Dynamic shear modulus: G*= G'+iG''



- Thermal aging at different temperatures

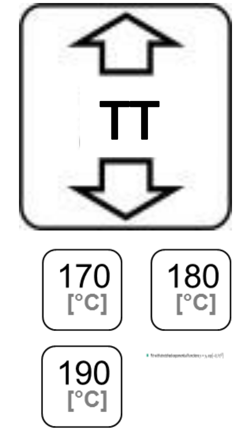
E_A = 68 kJ/mol



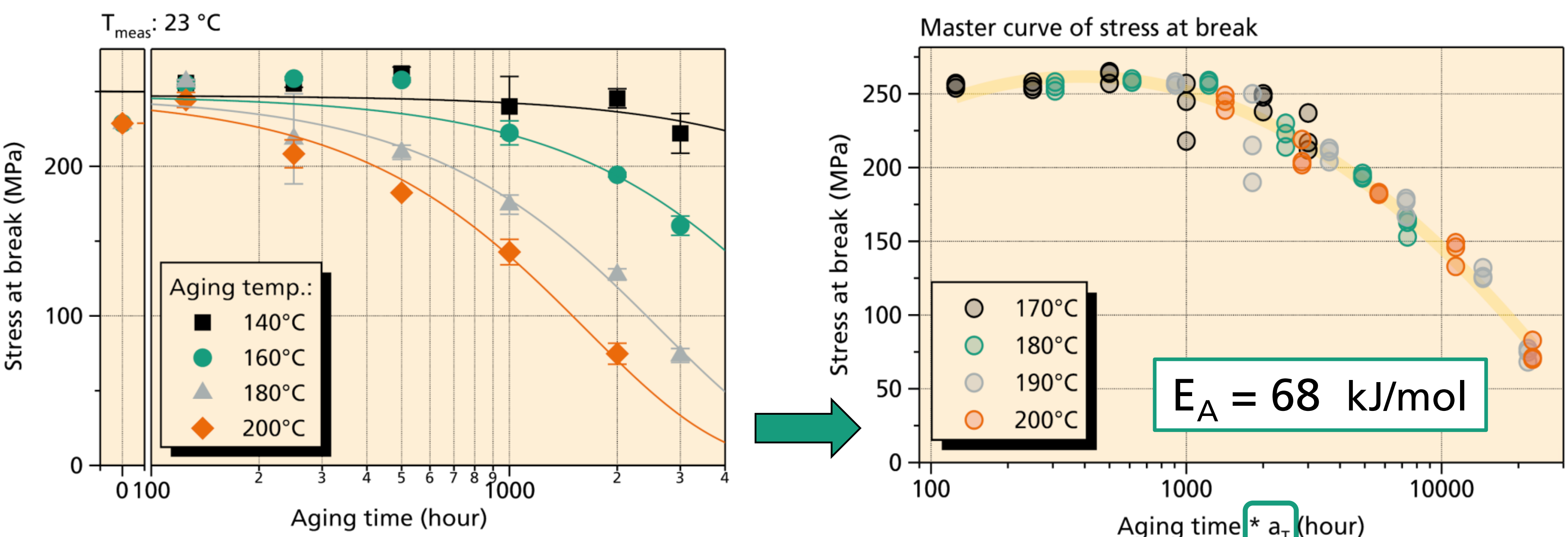


Chemo-crystallization?

Tensile test
Stress at break



- Fit with stretched exponential functions $y = y_0 \exp\left(-(t/\tau)^{\beta}\right)$



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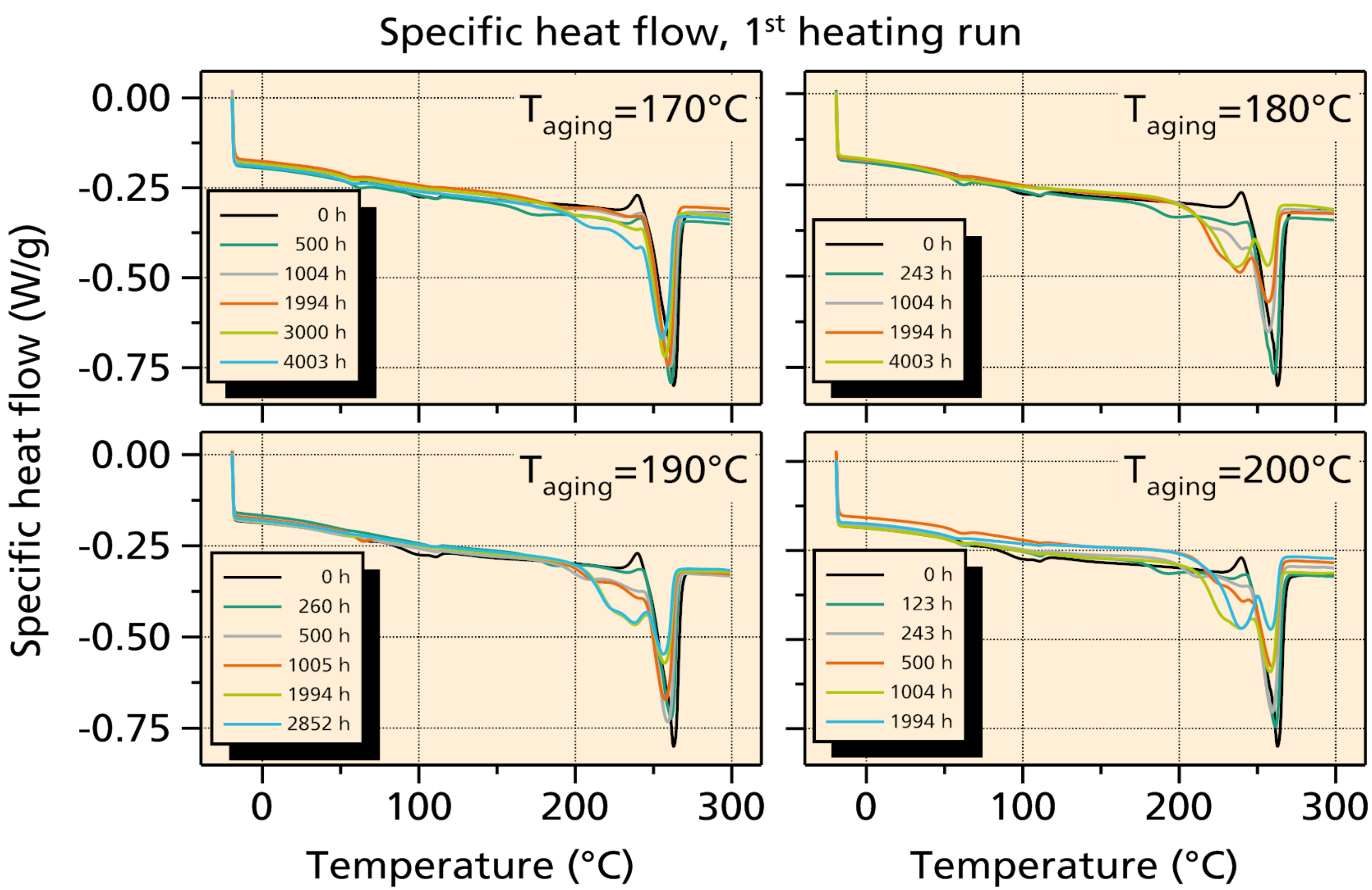
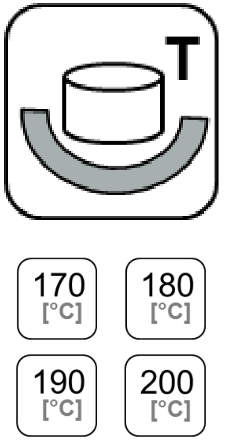
Thermal Analysis
DSC

- Melting

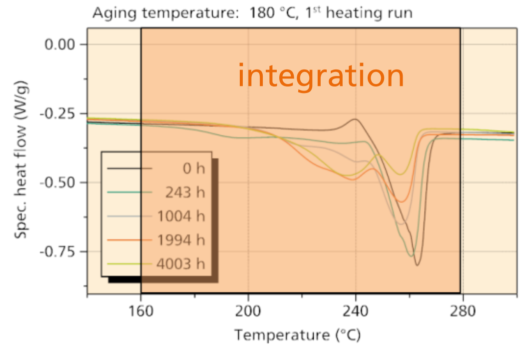


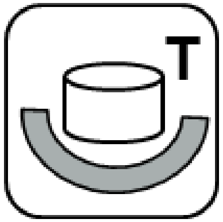


Fraunhofer LBF

Thermal Analysis

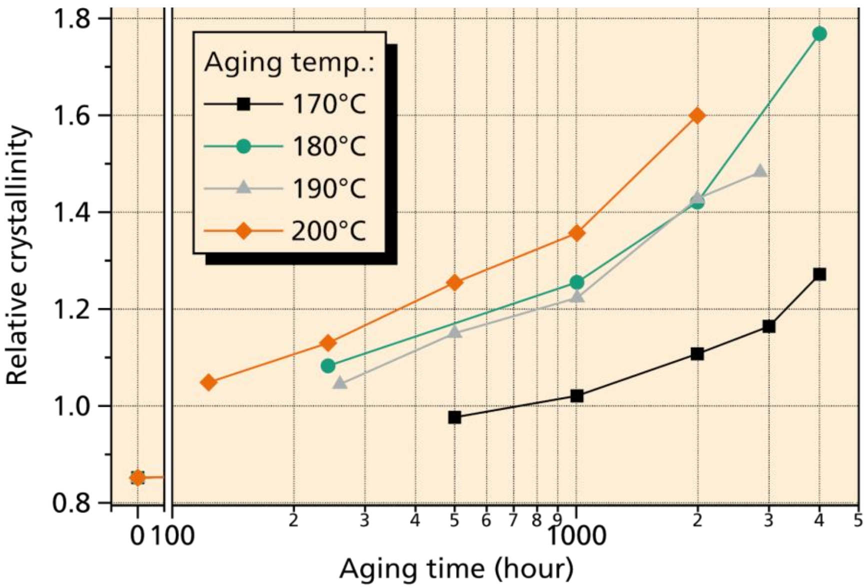
DSC

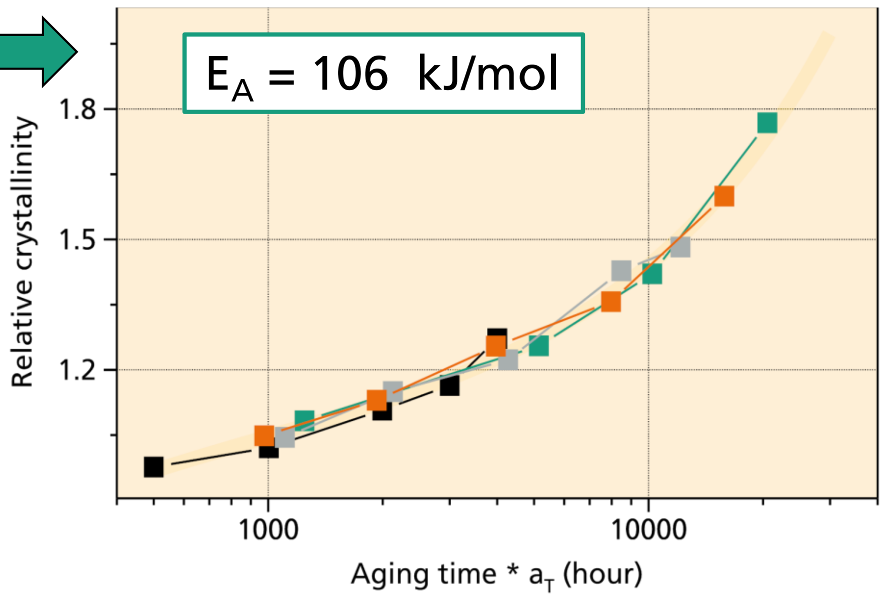




170 [°C] | 180 [°C] | 190 [°C] | 200 [°C]

- Relative crystallinity:
  Quotient of melting enthalpies of first and second heating

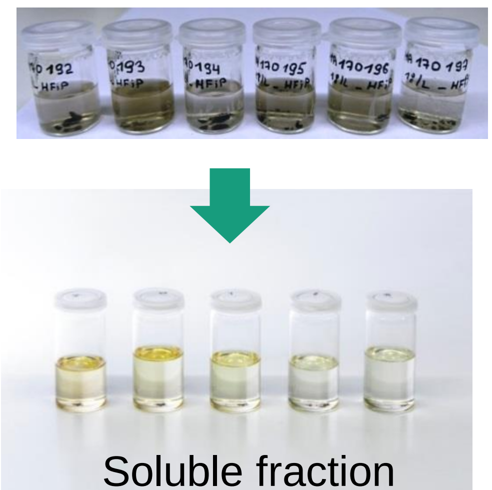




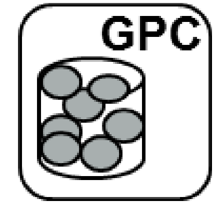
Methods

Chemical Analysis

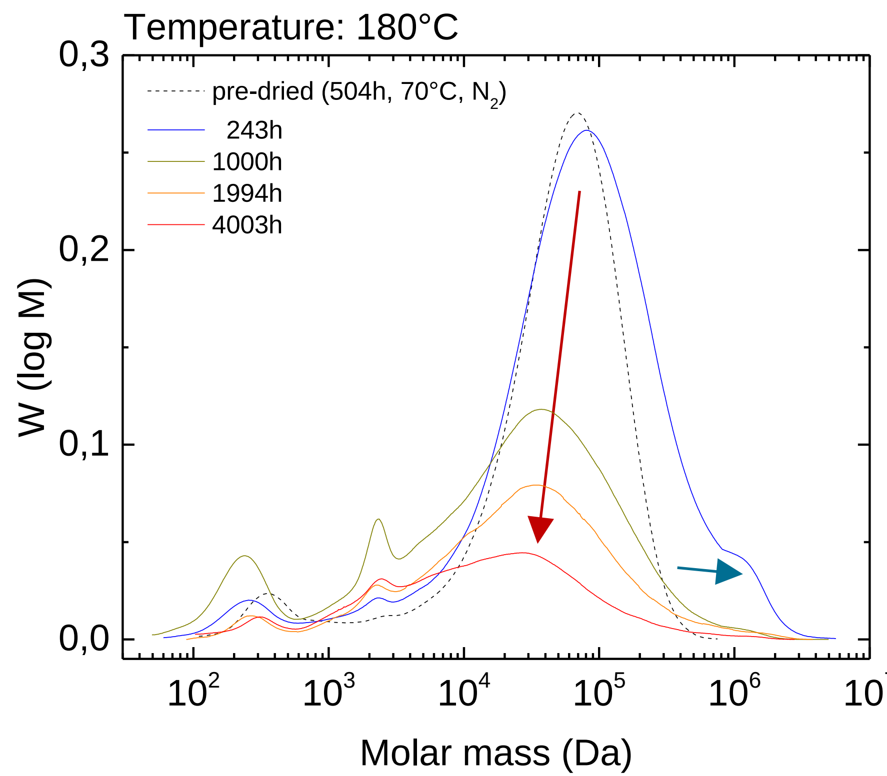
- GPC
- TGA
- MALDI-ToF-MS
- NMR
- FTIR



Gel permeation chromatography



180
[°C]

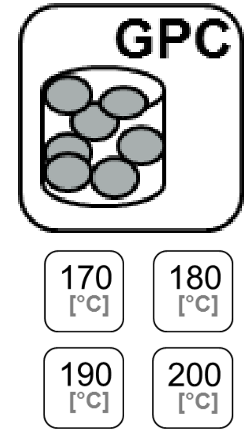


Interplay of branching and chain scission

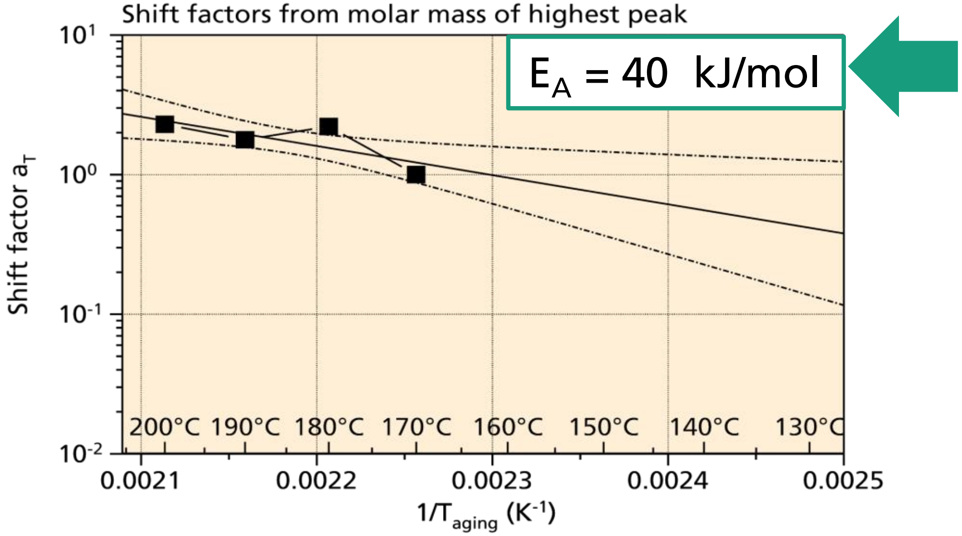
Fraunhofer LBF

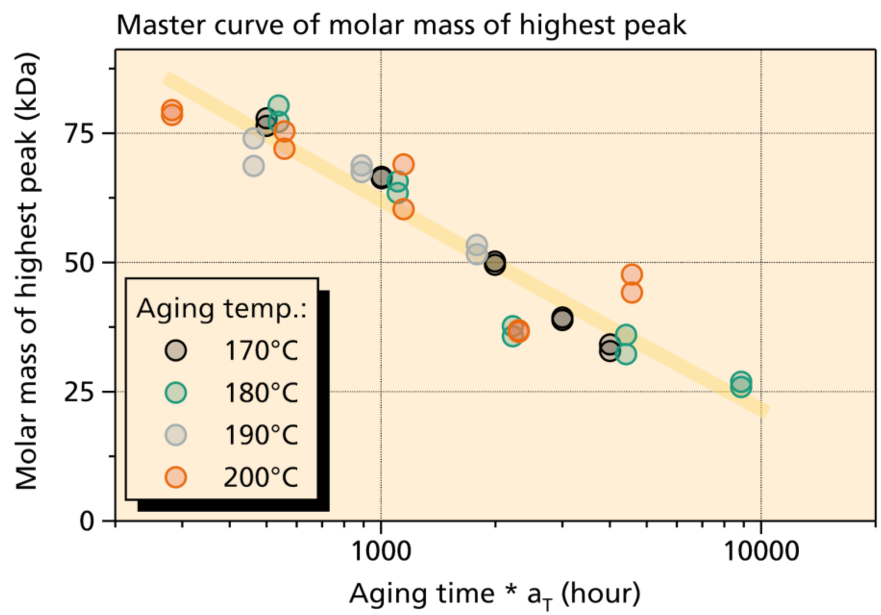
GPC Results

Molar mass (M_{max})



- Mainly chain scission





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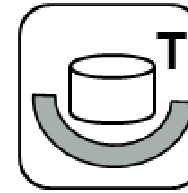
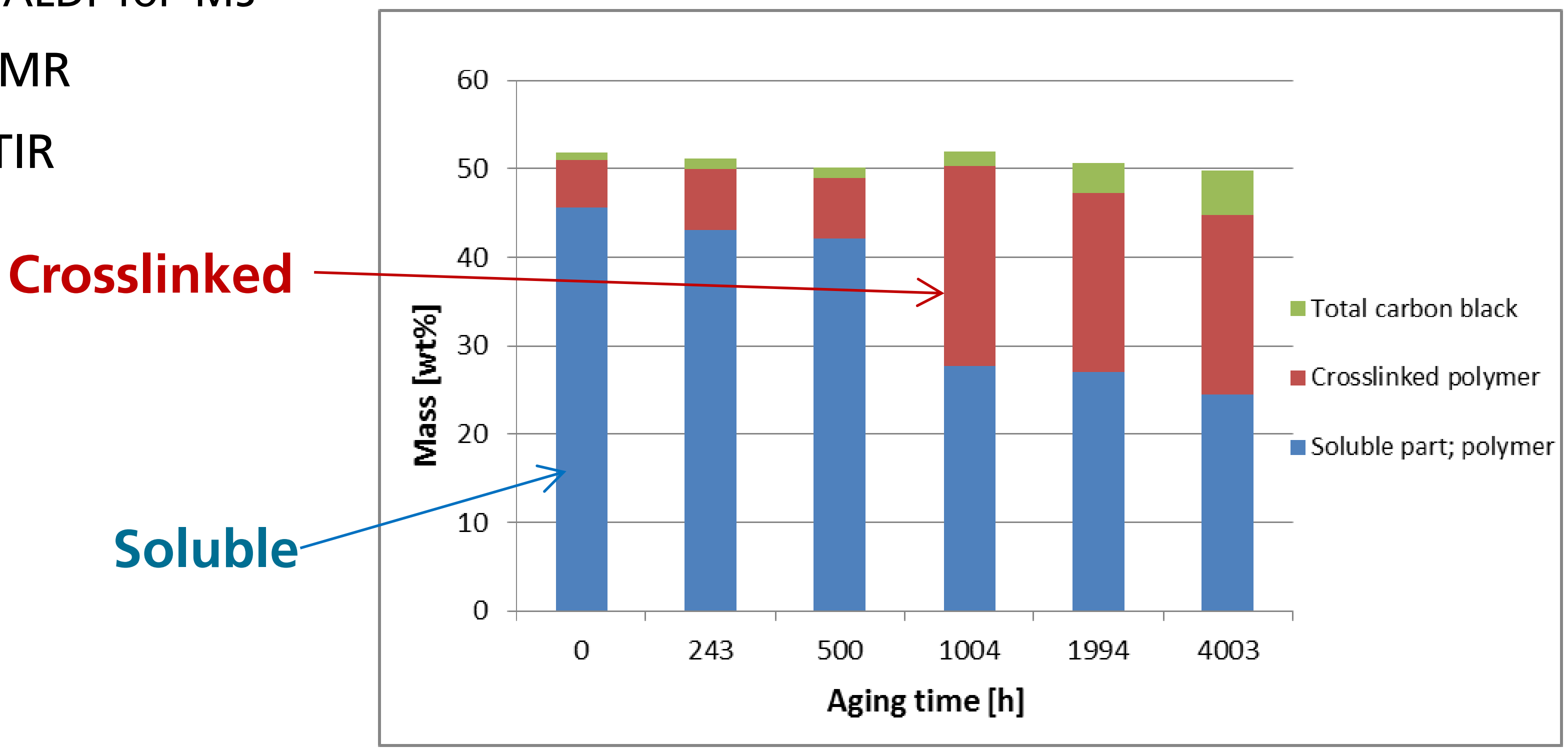
Methods
Thermogravimetry (TGA)



180
[°C]

- GPC
- TGA
- MALDI-ToF-MS
- NMR
- FTIR

Indication of crosslinking



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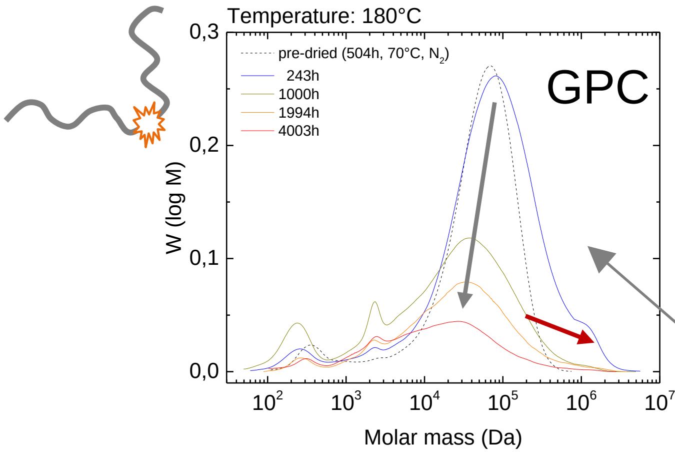
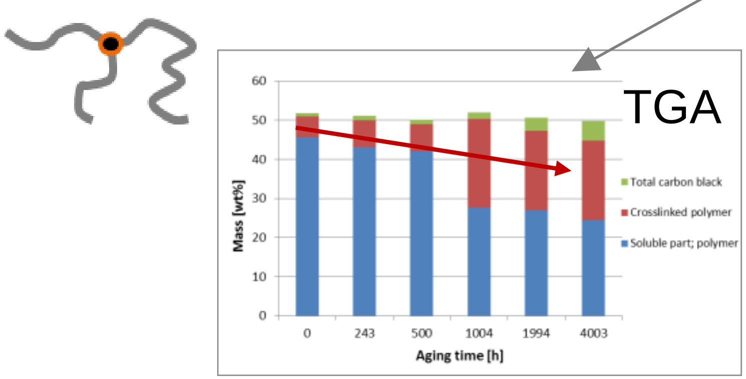
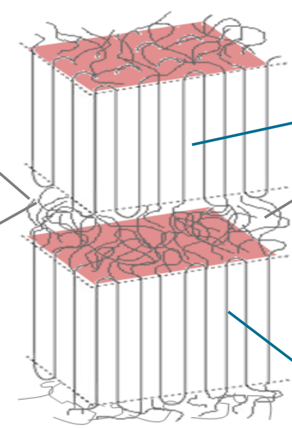
Aging mechanisms and suitable test methods

Chemical structure

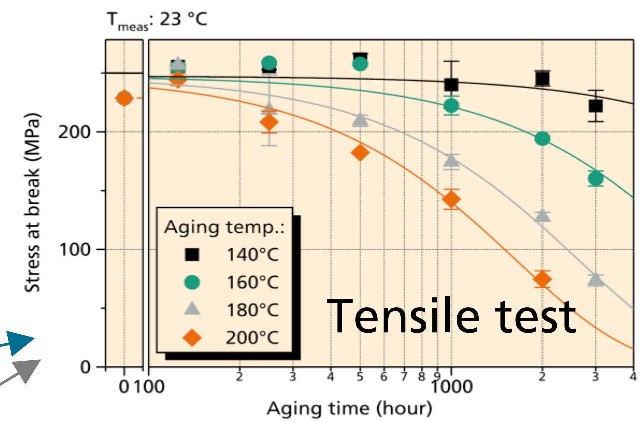




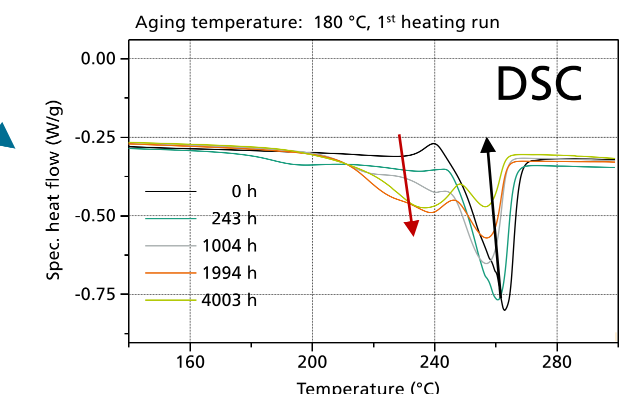
Thermal aging



Mechanical properties



Crystalline structure



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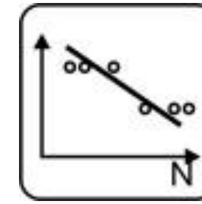
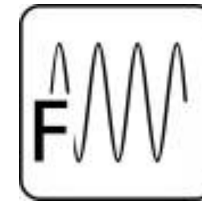
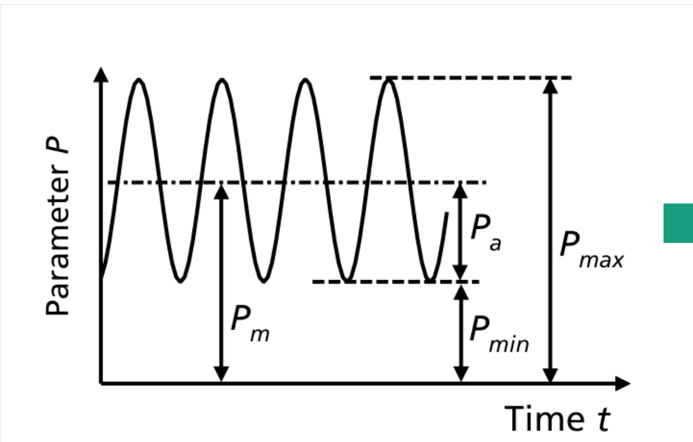
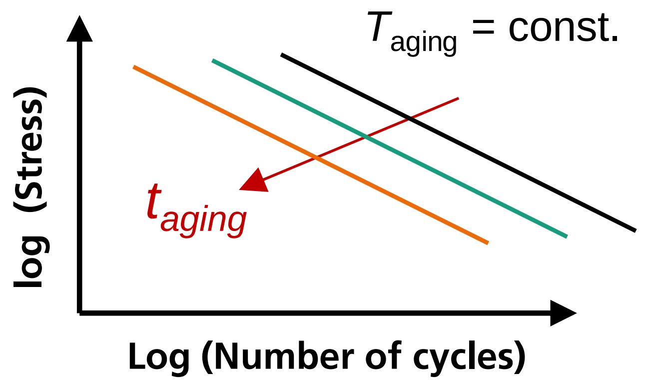
Methods
Cyclic fatigue testing



Stress-number (S/N) curves



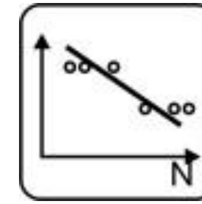
R-ratio: $R = P_{min} / P_{max}$; $R_F \approx 0$

→ Numbers of cycles to failure

Stress amplitude: 20 – 42 MPa

Cyclic Fatigue

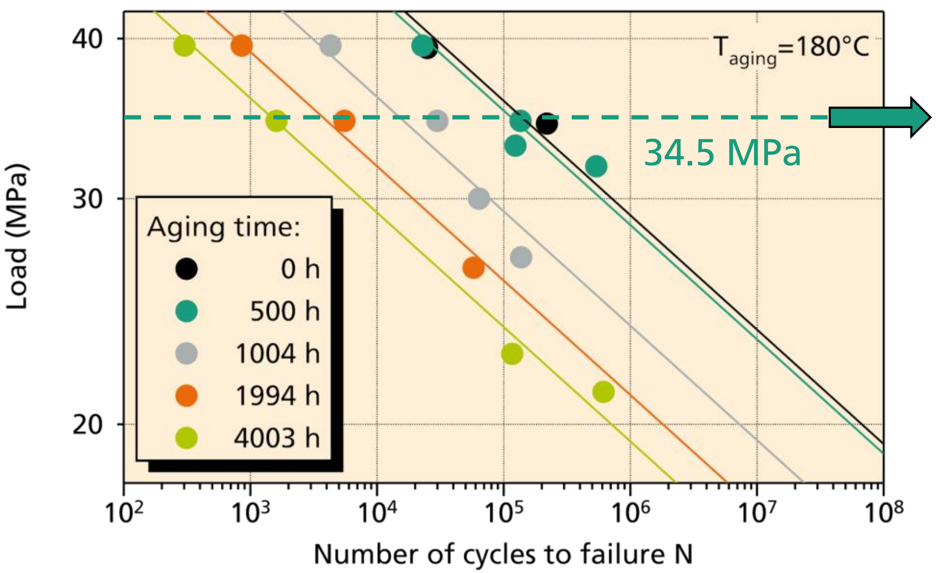
S-N Curves for different aging times



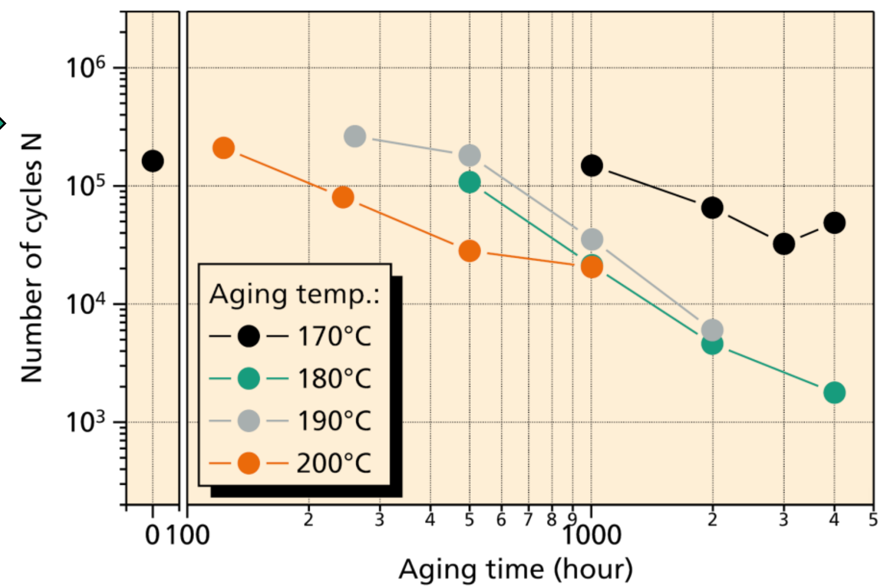
- Number of cycles to failure
- Analysis for constant load (34.5 MPa)

170 [°C] | 190 [°C] | 180 [°C] | 200 [°C]

Different aging times



Different aging temperatures

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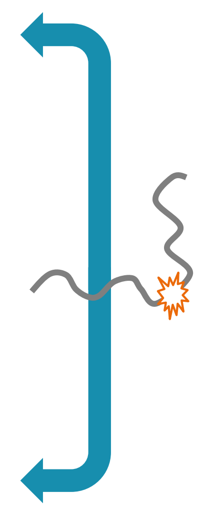
<u>Different</u> apparent activation energies for different experimental quantities

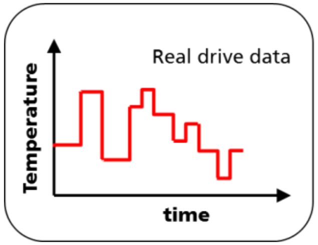
	Method	Quantity	Ea (kJ/mol)
Mechanical properties	Shore hardness	Shore D	55 - 80 kJ/mol
	Impact test	Impact energy	
	Tensile test	Strain at break	
		Stress at break	
	DMA	Shear modulus @150°C	
Fatigue	Cyclic fatigue	No of cycles @ 34.5 MPa	≈100 kJ/mol
Crystalline structure	DSC	Relative crystallinity	≈105 kJ/mol
Chemical structure	GPC	Mw	≈50 kJ/mol



D. Lellinger, I. Alig, H. Oehler, , K. Rode, F. Malz, L.M. Herkenrath, J. Y. Youn; Accelerated thermal aging of thermoplastic materials for the motor compartment: Characterization, degradation model and lifetime prediction, in: Service Life Prediction of Polymers and Coatings, Enhanced Methods, Edited by C.C. White, M.E. Nichols, J.E. Pickett, ch. 8, Elsevier 2020, p.116 -160, (ISBN 978-0-12-818367-0).

Equivalent aging times for isothermal aging experiments (oven temperature 170 °C) for different properties

- Real drive data

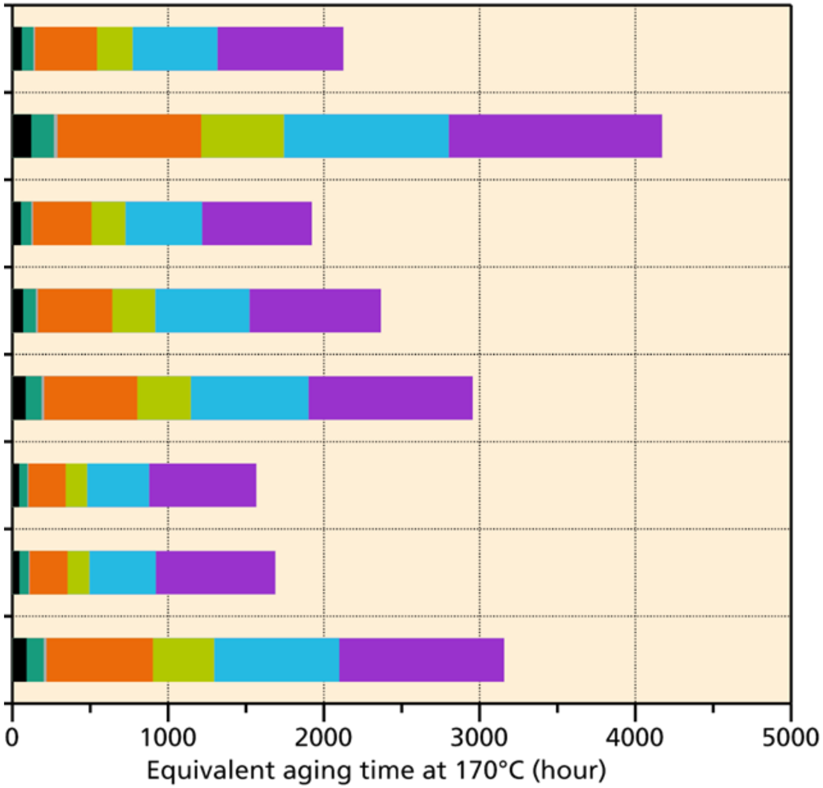


- Apparent activation energies for the different methods

$$a_T = a_{T,0} \exp\left(\frac{-E_a}{RT}\right)$$

Properties

Different driving modes



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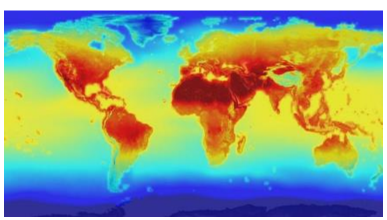
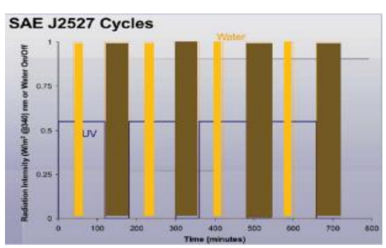
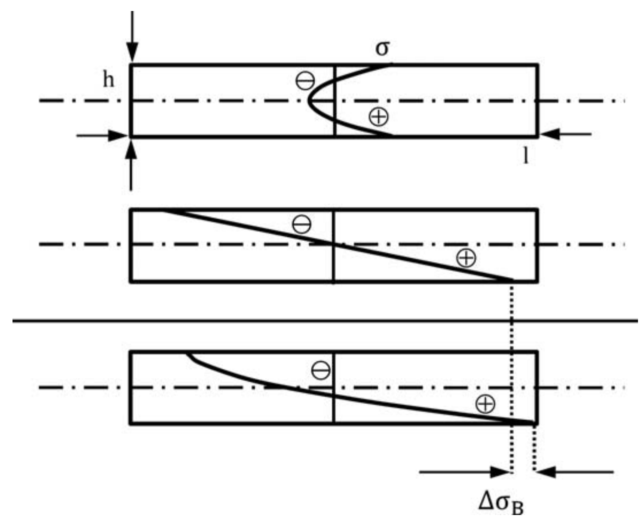
Example 2
Modelling: “Simulated” weathering of PMMA

- Outdoor data and accelerated weathering protocols
- Calculation of thermal and hygroscopic stresses → failure







Moisture-induced stress

Thermal stress

Superposition

G. Geetz, J. Wieser, I. Alig, G. Heinrich
Polymer Eng.Sci. 2016, DOI 10.1002/pen

A. Neumann, D.Lellinger, A. Bülow, H.Oehler, I. Alig, **Simulation von Sorption und mechanischen Spannungen in Thermoplasten unter Verwendung von Wetterdaten und Bewitterungsprotokollen,** 49. Jahrestagung der Gesellschaft für Umweltsimulation - GUS, Tagungsband, Stutensee-Blankenloch 2021

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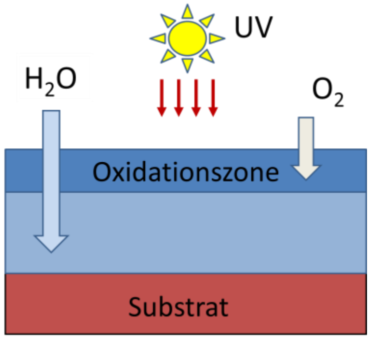
Zusammenfassung und Ausblick

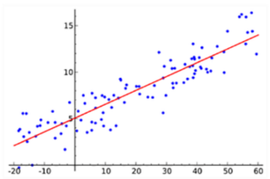
„Lebensdauervorhersagen sind schwierig, wenn sie Kunststoffe betreffen."

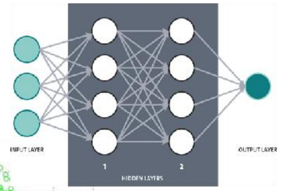
… aber es gibt Hoffnung

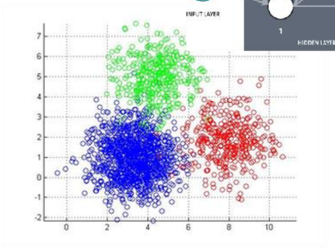
- Notwendigkeit der Verbesserung der Modelle (Kinetik und Materialeigenschaften)
- Die Parametrisierung der Modele ist zeit- und kostenaufwändig
- Standortbezogene Wetterdaten sind gut zugänglich
- Es ist schwierig, Betriebs- und Mikroklimadaten zu erhalten



Degradations- und Versagensmodelle







KI-Methoden

Referenzen

A. Neumann, D.Lellinger, A. Bülow, H.Oehler, I. Alig,
Simulation von Sorption und mechanischen Spannungen in Thermoplasten unter Verwendung von Wetterdaten und Bewitterungsprotokollen,
49. Jahrestagung der Gesellschaft für Umweltsimulation - GUS, Tagungsband, Stutensee-Blankenloch 2021 (im Druck)

T. Lellinger, I. Alig, H. Oehler, , K. Rode, F. Malz, L.M. Herkenrath, J. Y. Youn;
Accelerated thermal aging of thermoplastic materials for the motor compartment: Characterization, degradation model and lifetime prediction,
in: Service Life Prediction of Polymers and Coatings, Enhanced Methods, Edited by C.C. White, M.E. Nichols, J.E. Pickett, ch. 8, Elsevier 2020, p.116 -160, (ISBN 978-0-12-818367-0).

D. Lellinger, T. Kroth, N. Reinhardt, T. Bitsch, K. Kühne, K. Rhode, F. Malz, M. Wallmichrath, I. Alig;
Combination of material characterization and cyclic fatigue testing for investigation of elastomer aging,
in: Service Life Prediction of Polymers and Outdoor Weathering, Edited by C.C. White, M.E. Nichols, J.E. Pickett, Elsevier 2017, p. 197-227 (ISBN: 970-3-2349-7763).

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Vielen Dank für die Aufmerksamkeit!
Haben Sie Fragen?

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3. März

Schadensanalyse mit modernster instrumenteller Analytik

22. April

Rezyklate aus dem gelben Sack
- *Potenzial für hochwertige Kunststoff-anwendungen*

6. Mai

Lebensdauer von Kunststoffen effizient vorhersagen
- *Ermüdungsversuche*
- Schadenshypothesen
- Modellierung

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