

Oxidative lifetime prediction of polypropylene geotextiles in an aqueous medium by using high-pressure autoclave tests

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COLLOQUIUM 607

MARINE AGING OF POLYMERS

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Agenda

Examples of geotextiles in marine applications

Question:

When will the End-of-Life of a geotextile be reached?

High-pressure autoclave testing (HPAT)

- Test setup
- Test conditions

Test results of a GTX-W

- HPAT test results
- Extrapolations regarding T and $p(O_2)$

Service life estimation

Summary



Woven geotextile (GTX-W)

Geotextiles in marine engineering

Chris R. Lawson (2016) in Geotextiles – From Design to Applications

- Geotextile containment units
 - Geotextile bags
 - Geotextile tubes (container)
- Marine revetments
- Containment dykes
- Protection dykes
- Artificial reefs
- Offshore engineering applications
 - Scour protection for offshore wind turbines
 - Support and protection for offshore pipelines

Jamuna-Meghna river

Erosion mitigation project, Bangladesh



Source: Heilbaum/Oberhagemann

Jamuna-Meghna river

Erosion mitigation project, Bangladesh

SKZ



Source: Heibaum/Oberhagemann

Jamuna-Meghna river



Erosion mitigation project, Bangladesh



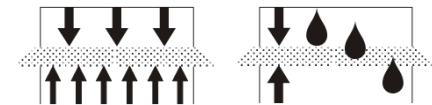
Source: Heibaum/Oberhagemann

Geotextile bags



Source: Naue

Geotextile bag revetment



Geotextile bags for coastal protection

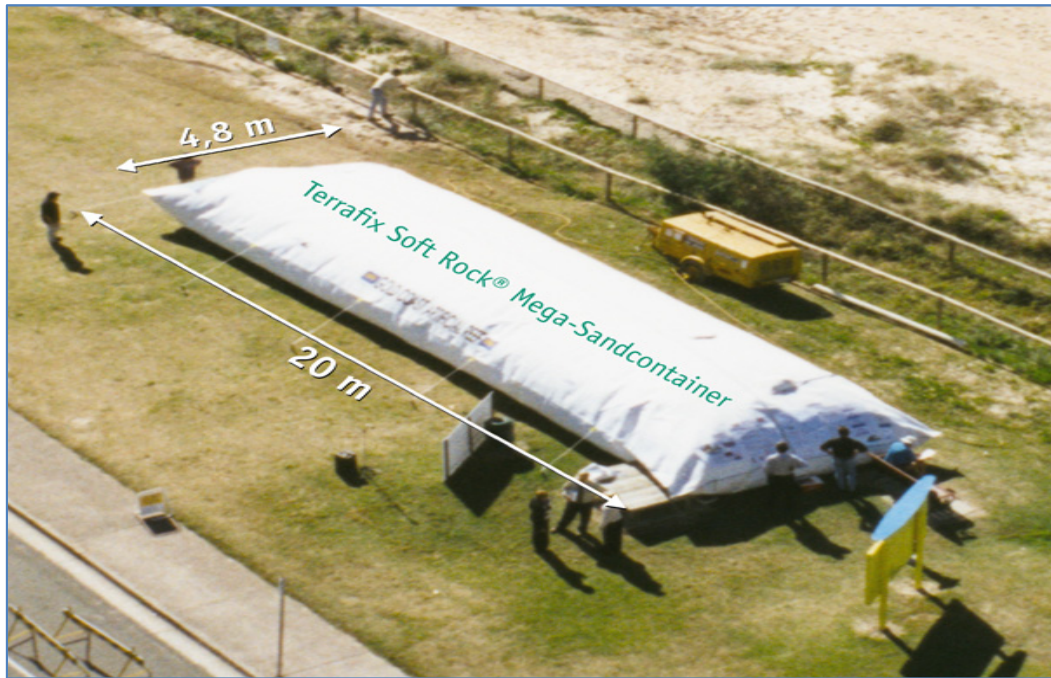


Geotextile container revetment



Source: TenCate

Artificial reefs with **geotextile containers** for erosion control and surf management



Geotextile containers for coastal protection

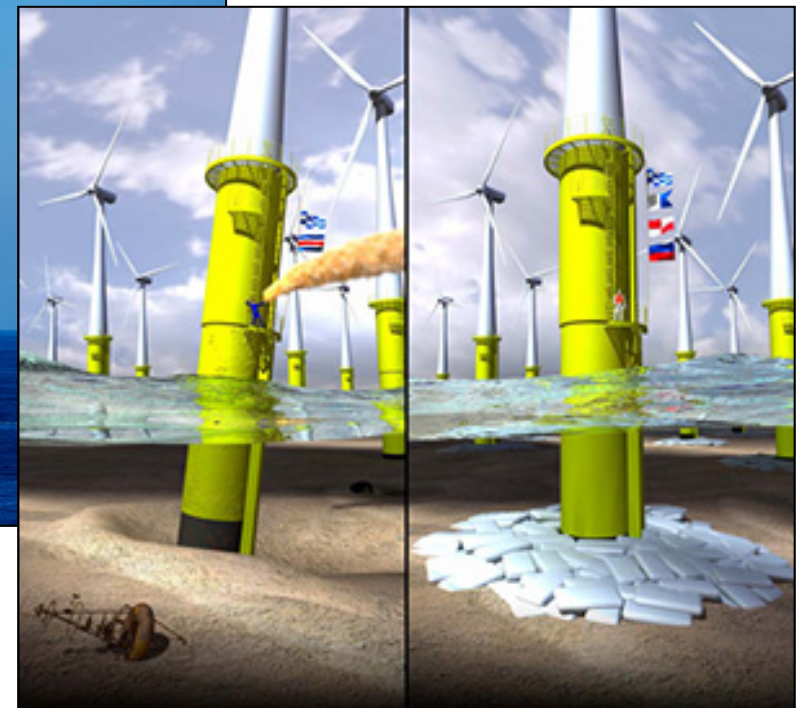


Sunlight exposed geotextiles

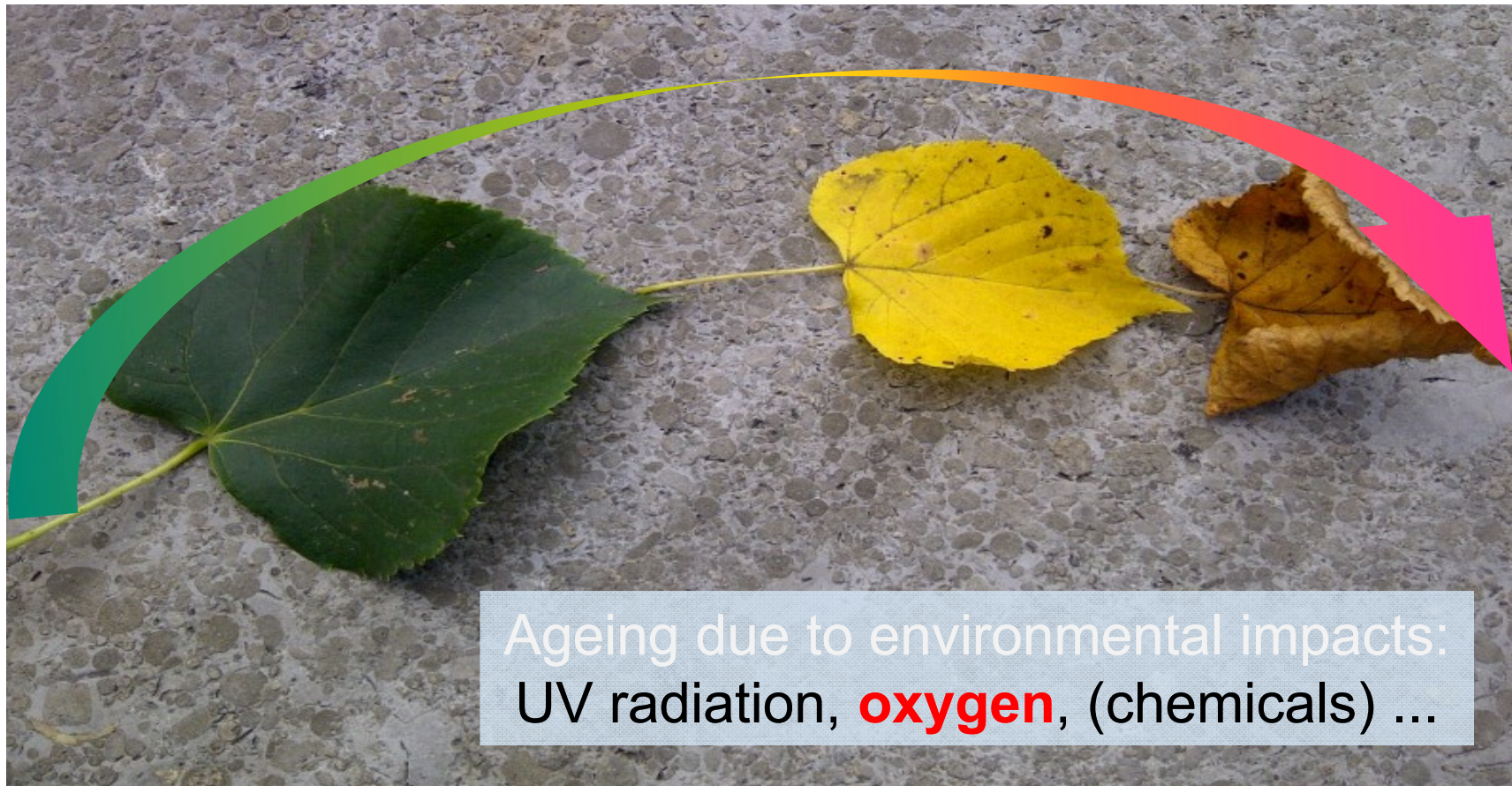


NOTE:
**UV-resistance
of exposed geotextiles
is limited !**
They may last a few years only.

Scour protection for offshore wind turbines with **geotextile bags**



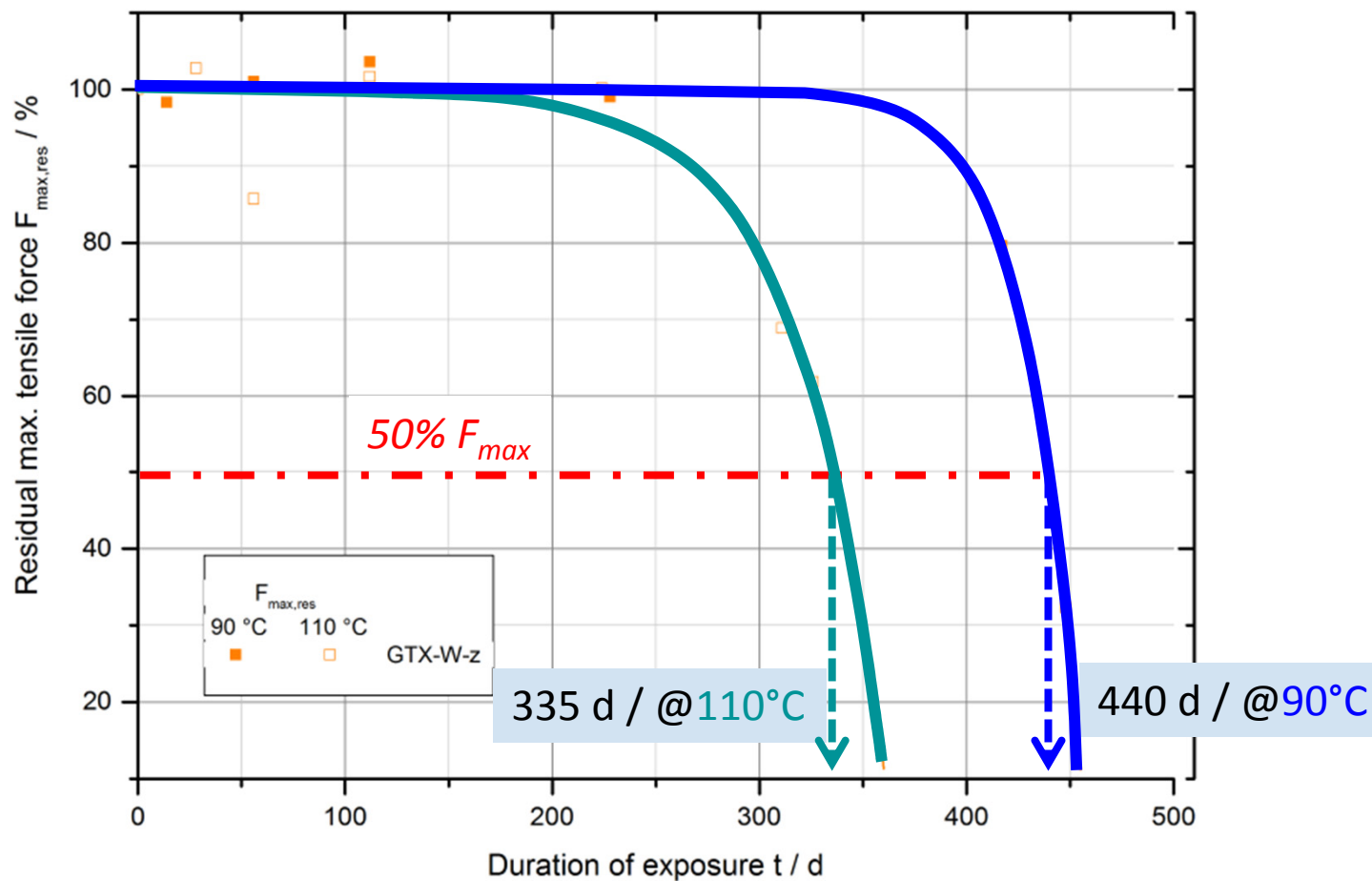
End-of-Life of PP-geotextiles



Ageing due to environmental impacts:
UV radiation, **oxygen**, (chemicals) ...

Woven geotextile

Oven test results



Simulation of Ageing in the Laboratory

- **Leaching tests**

wet ageing in water at elevated temperature

(pH-value, stirring, temperature tolerance, size of container, ...)

- **Oxidation tests**

dry ageing in air in laboratory oven at elevated temperature

(fresh-air intake, ventilation, circulation, air change rates, air velocity, temperature distribution, temperature tolerance, distance between specimens, volume of oven, ...)

- **High-pressure autoclave tests (HPAT)**

(screening tests acc. to ISO 13438)

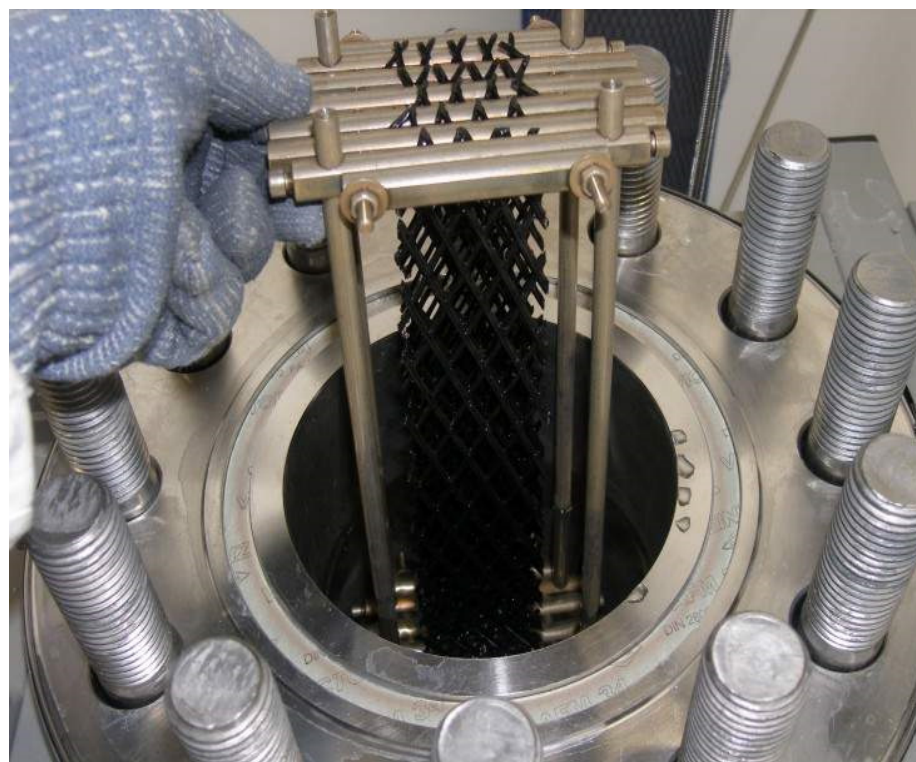
ageing in water at elevated temperature, elevated oxygen pressure and pH10

(stirring, temperature tolerance, size of autoclave, ...)

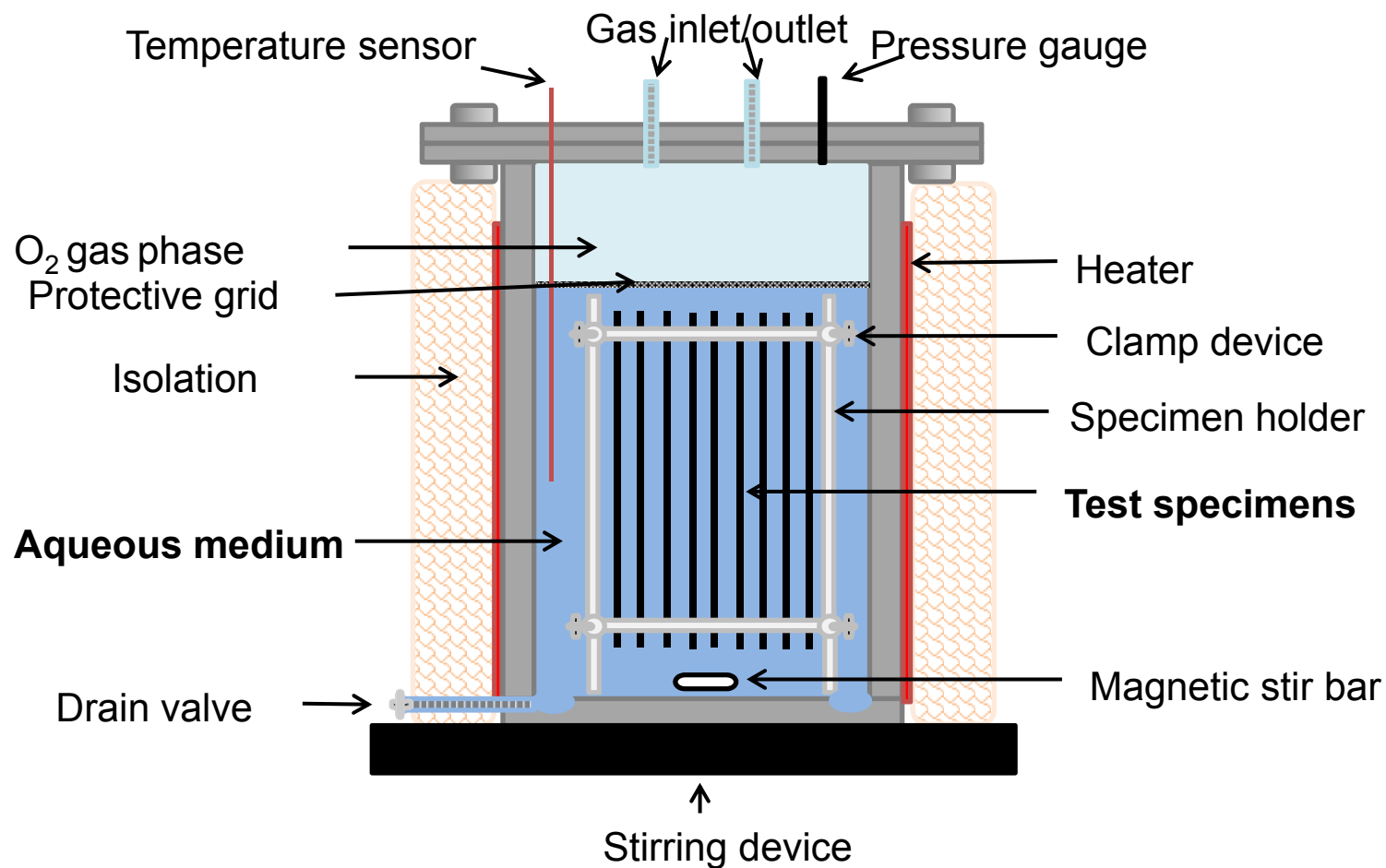
High-pressure autoclave test device

- **Test temperature:**
typically 60°C to 90°C
- **Oxygen pressure:**
typically 2 bar to 50 bar
- **Aqueous medium:**
typically 0.01M NaHCO₃ /
pH10 (alkaline)

- Acceleration due to
- **elevated temperature**
 - **availability of oxygen**
 - **aqueous medium**



High-pressure autoclave test device



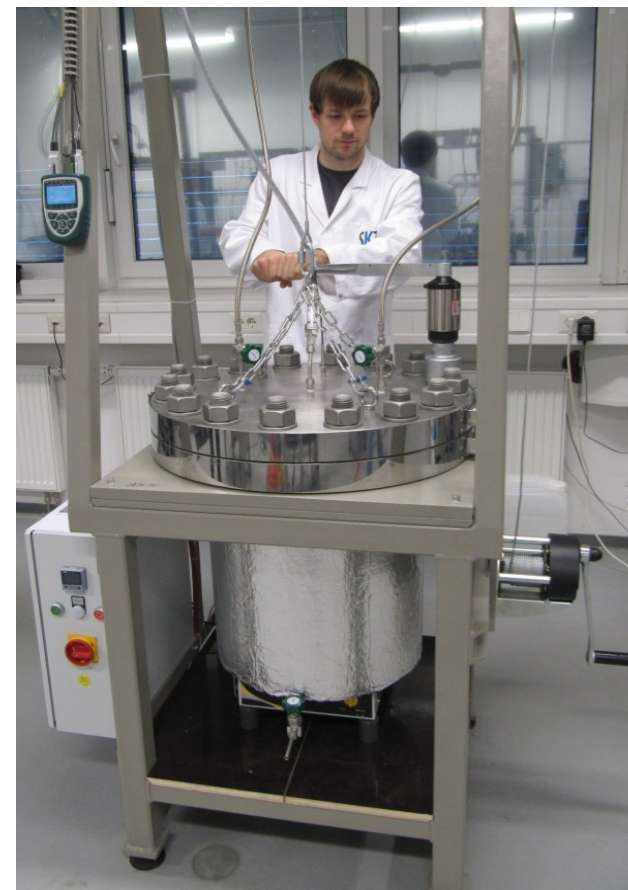


High-pressure autoclave test device

- Storage of samples in a high pressure autoclave
- Continuous recording of temperature and pressure
- Test temperature:
75 / 80 / 90 ° C
- Oxygen pressure:
0.4 / 0.9 / 2.0 / 3.0 / 5.0 bar

Note:

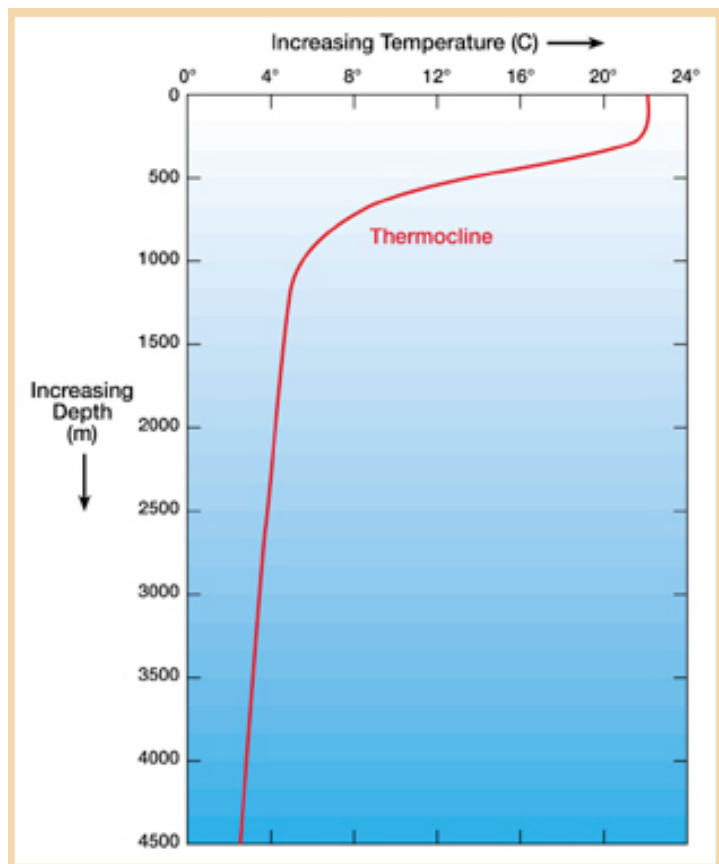
*The sample is tested in solid state
and not in melted state (as in OIT).*



Factor

TEMPERATURE

Temperature of Ocean Water



Note:

In some hot areas
the surface water temperature
in the sea may rise up to 35°C.

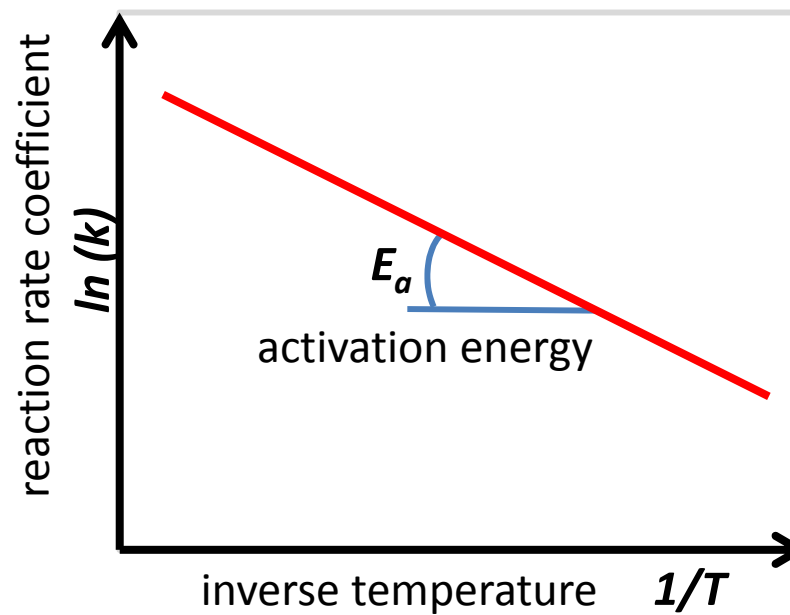
<https://www.windows2universe.org/?page=earth/Water/temp.html>

Svante Arrhenius



1903: Nobel Prize in chemistry

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

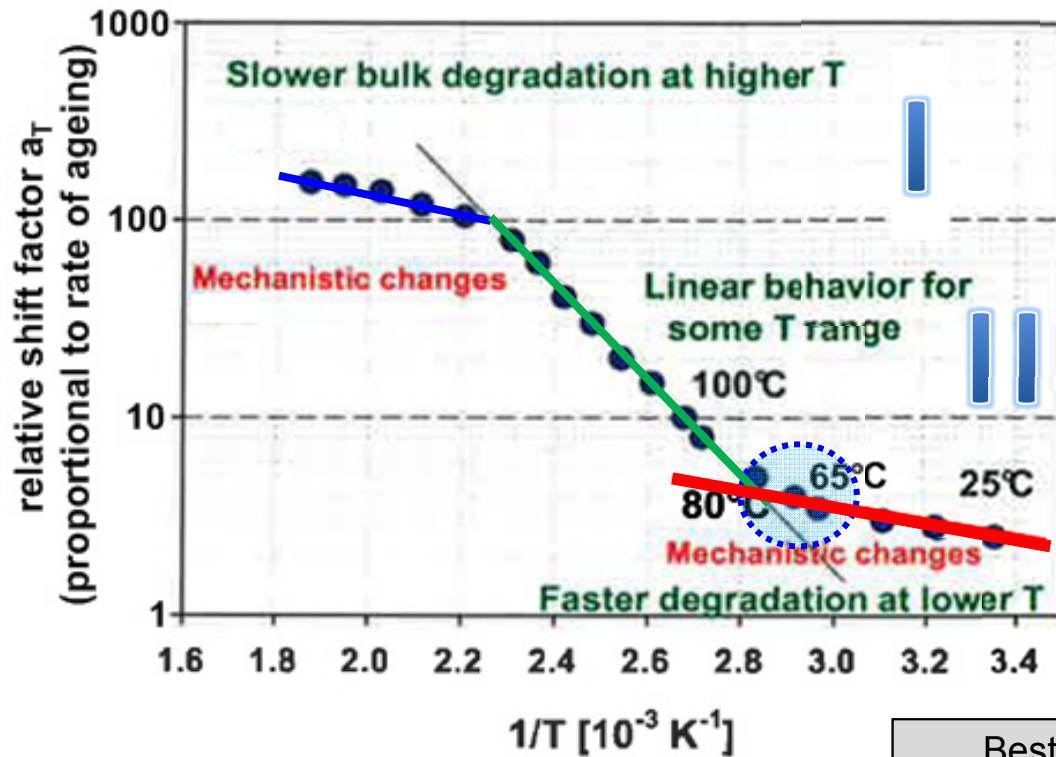


Studies through Europe



ARRHENIUS in Würzburg (1886/1887)

Temperature regime

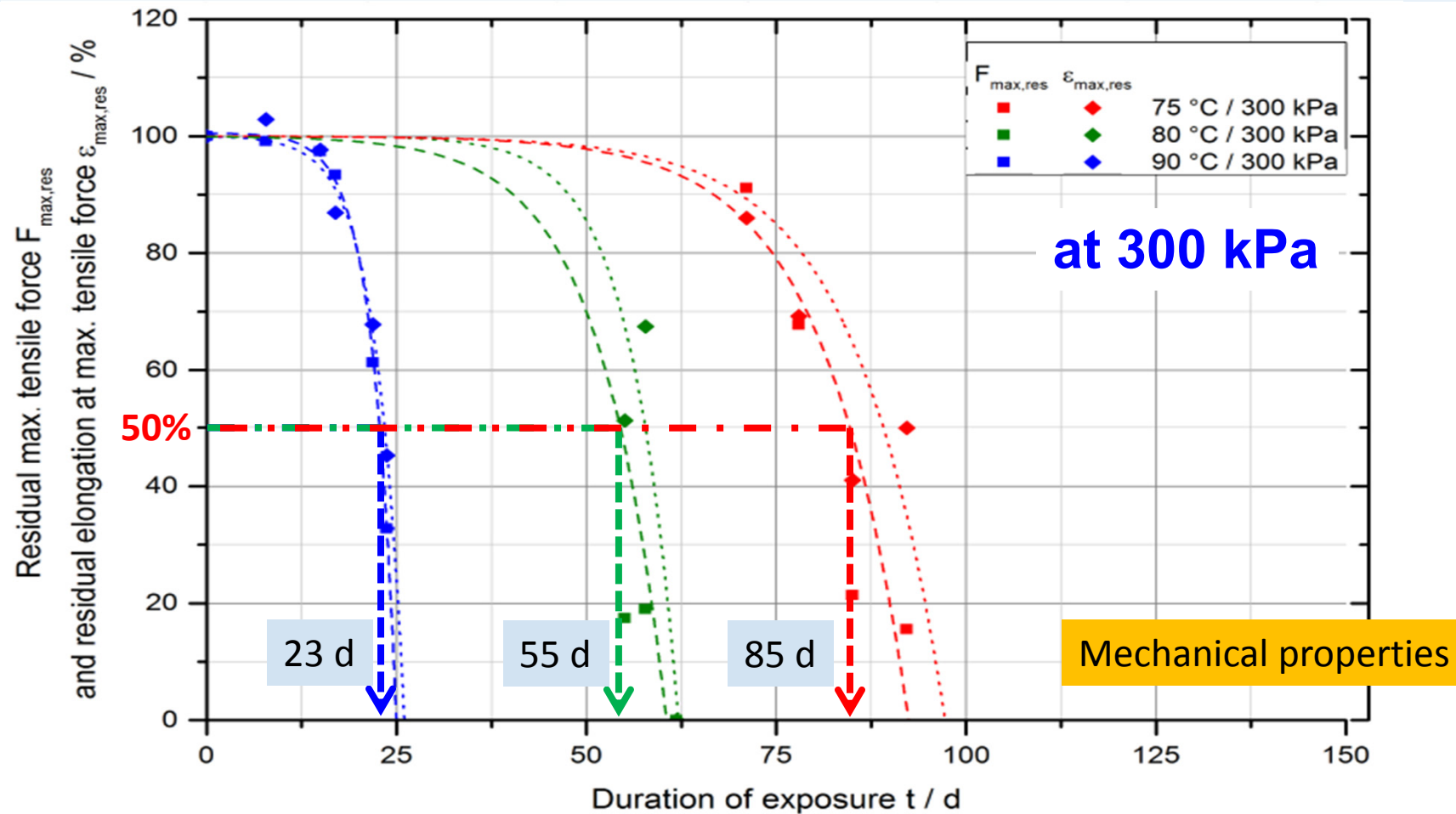


Müller & Jakob (2000):
 “80° C is the highest test temperature from which Arrhenius extrapolation to ambient temperatures is possible for PE”

Best laboratory practice for lifetime prediction:
 Ambient temperature + 40 K \geq Lowest test temperature

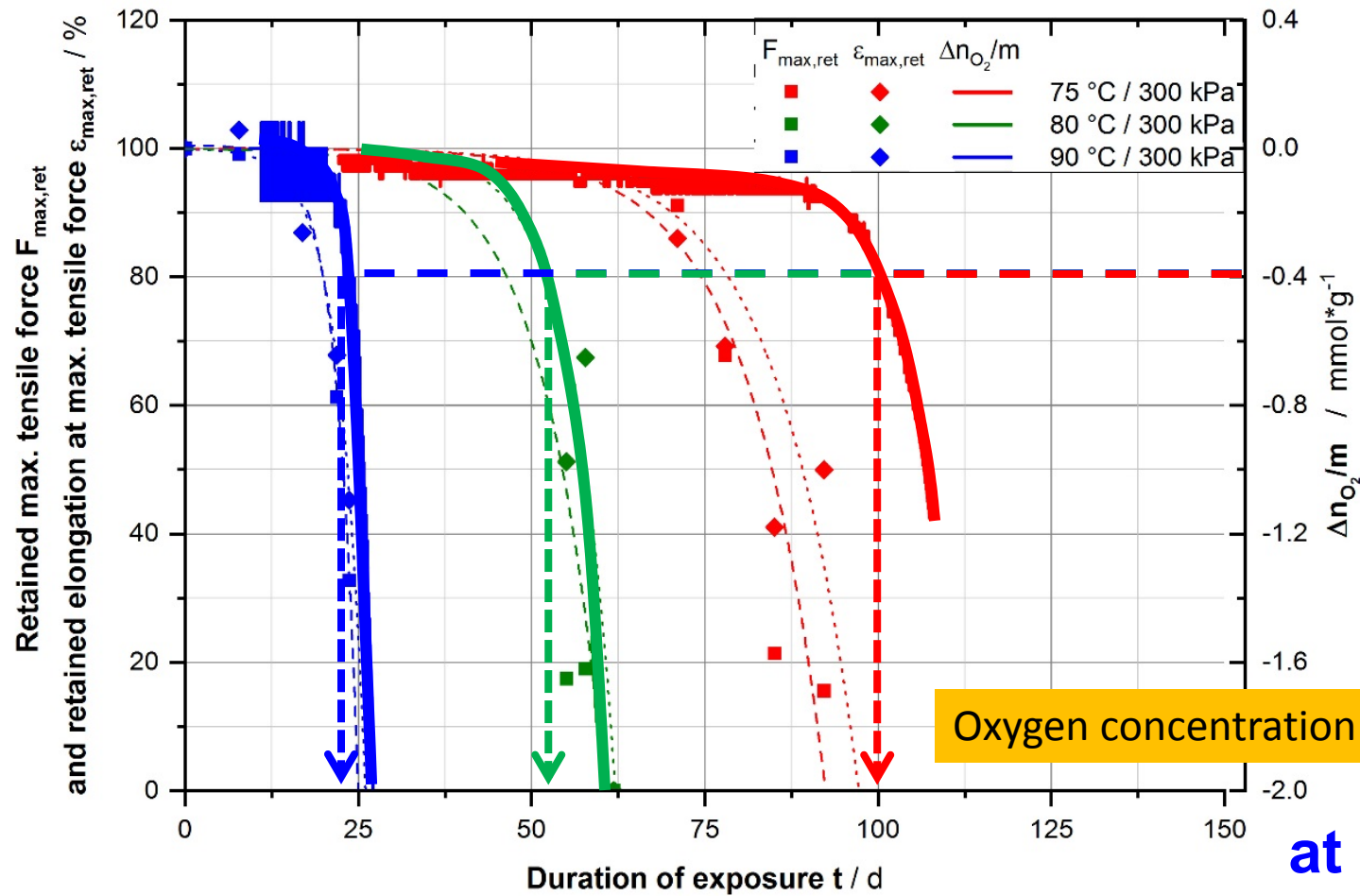
Woven geotextile

Autoclave test results at different T



Woven geotextile

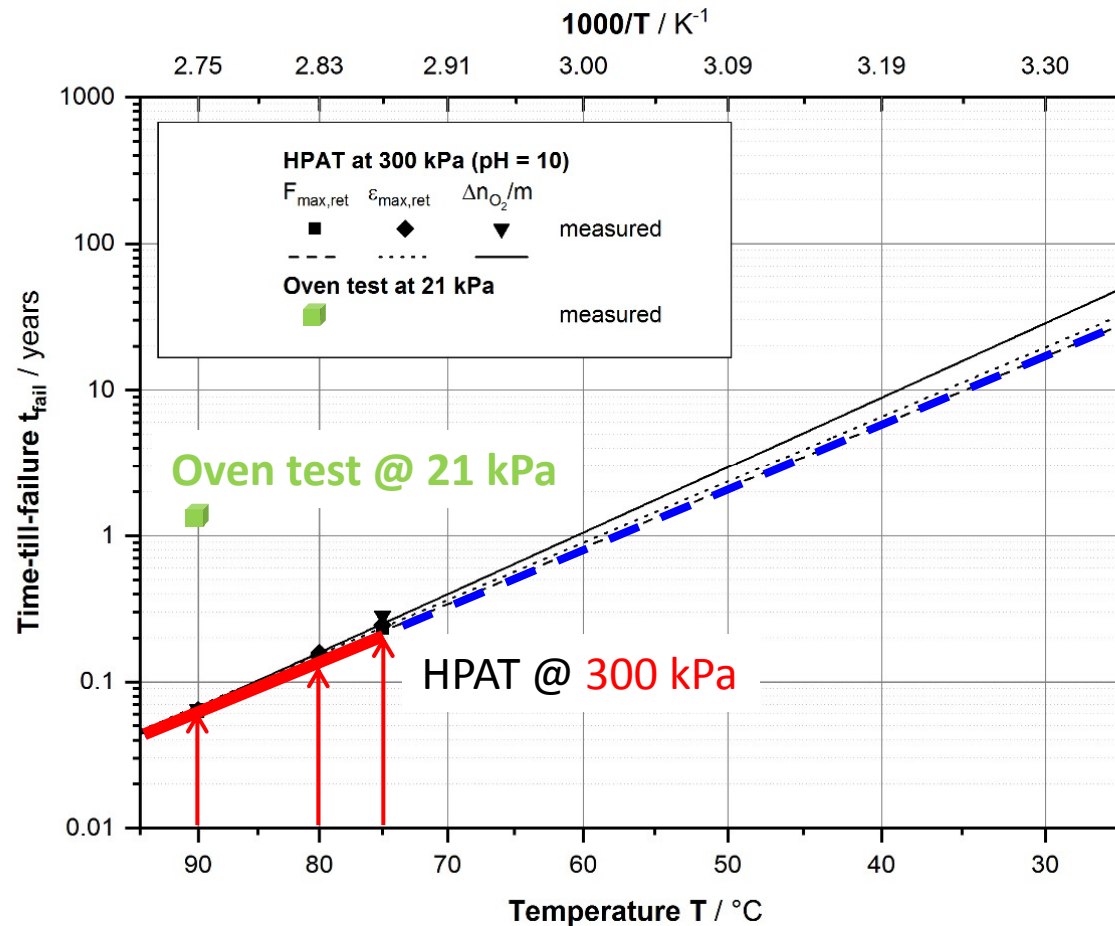
Autoclave test results at different T



at 300 kPa

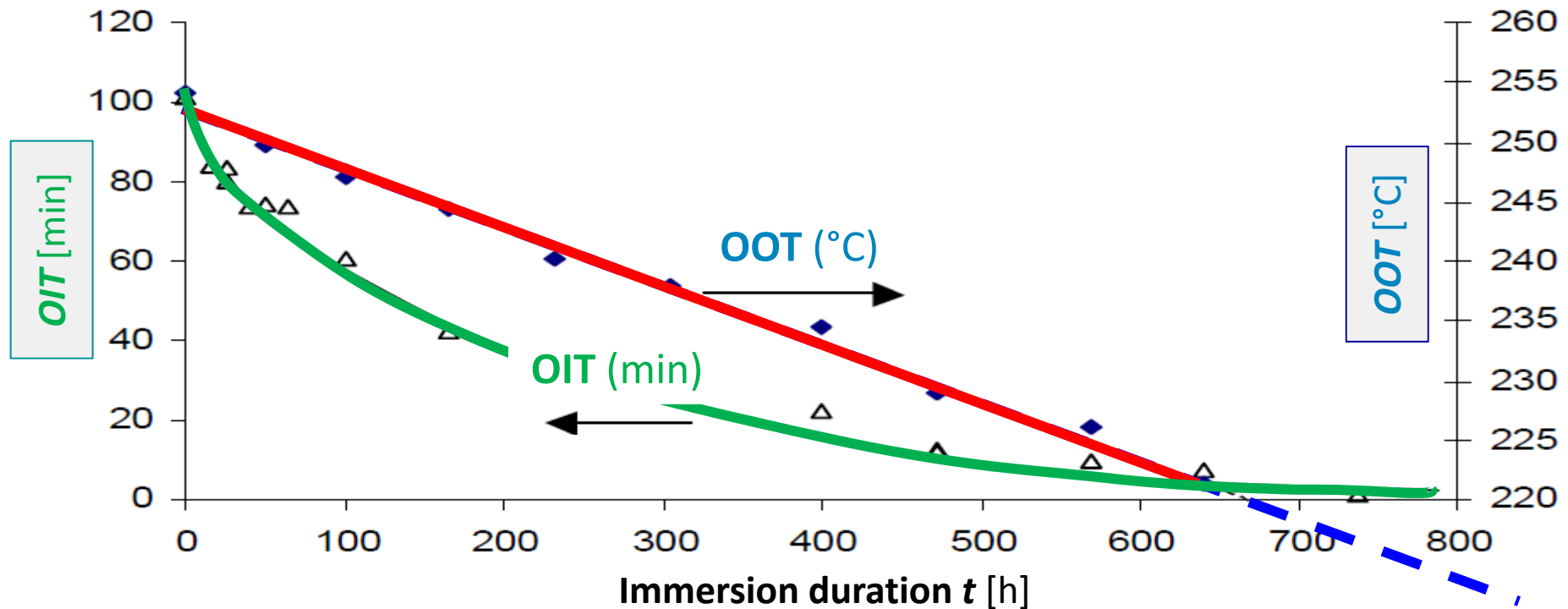
Woven PP-geotextile

Arrhenius-Extrapolation regarding temperature



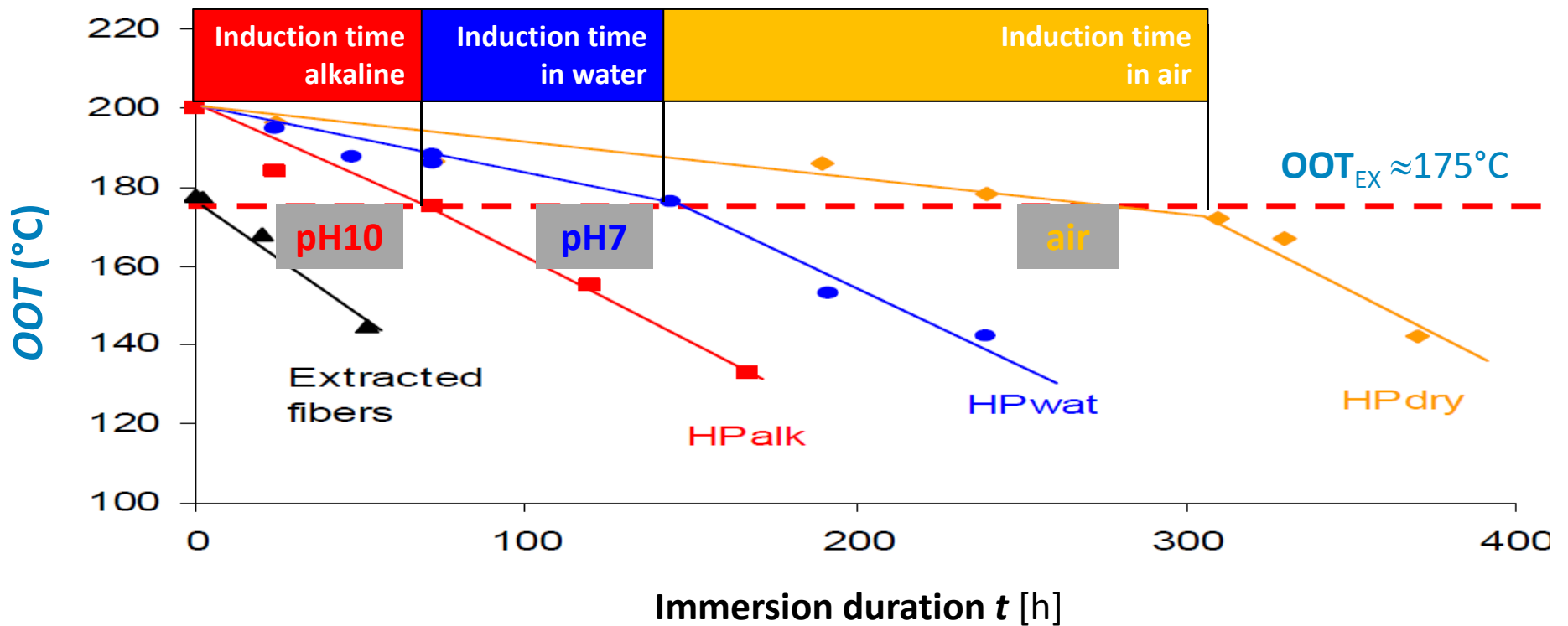
Factor
pH value

Geosynthetics stabilized with phenolic additives



Bartolomeo, Astruc, Massieu, Barberis, Lavaud & Benneton (2004).
 Thermo-oxidative ageing of polypropylene geosynthetics monitored by
 thermal analysis and mechanical tensile test.
 EuroGeo3, Munich, Germany

Geosynthetics stabilized with phenolic additives



Bartolomeo et al. (2004)

Suggestion

- **Study of influence on Antioxidant (AO) depletion by:**
 - Variation of pH-values (pH3, pH7 and pH10)
 - Effect of salt water

→ **Evaluation of depletion time of AO with the use of OOT**

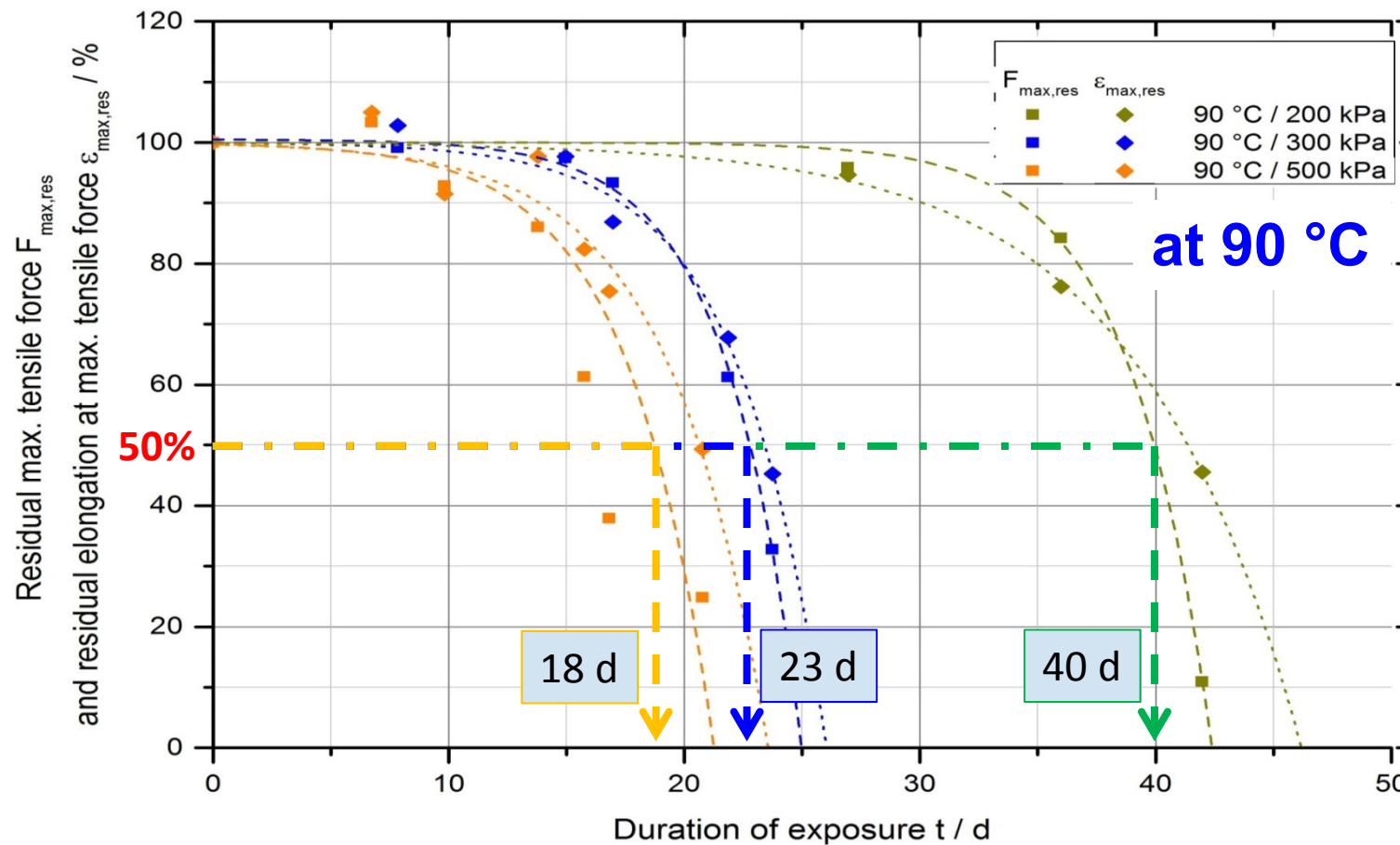
EN ISO 11357-6
*Differential scanning calorimetry (DSC) -
Determination of **Oxidation Induction Temperature (OOT)***

Factor

OXYGEN PRESSURE

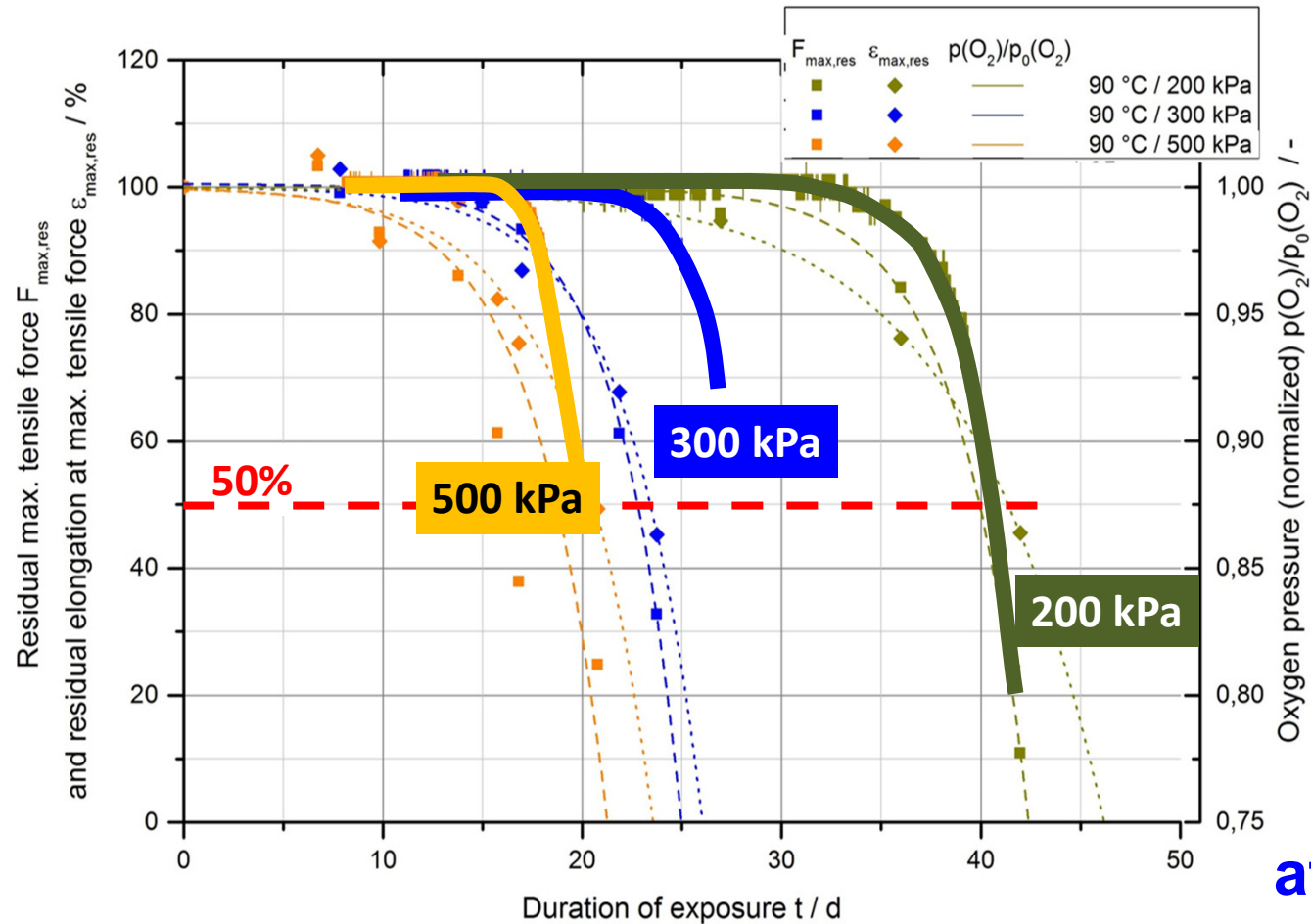
Woven geotextile

Autoclave test results at different O₂-pressure



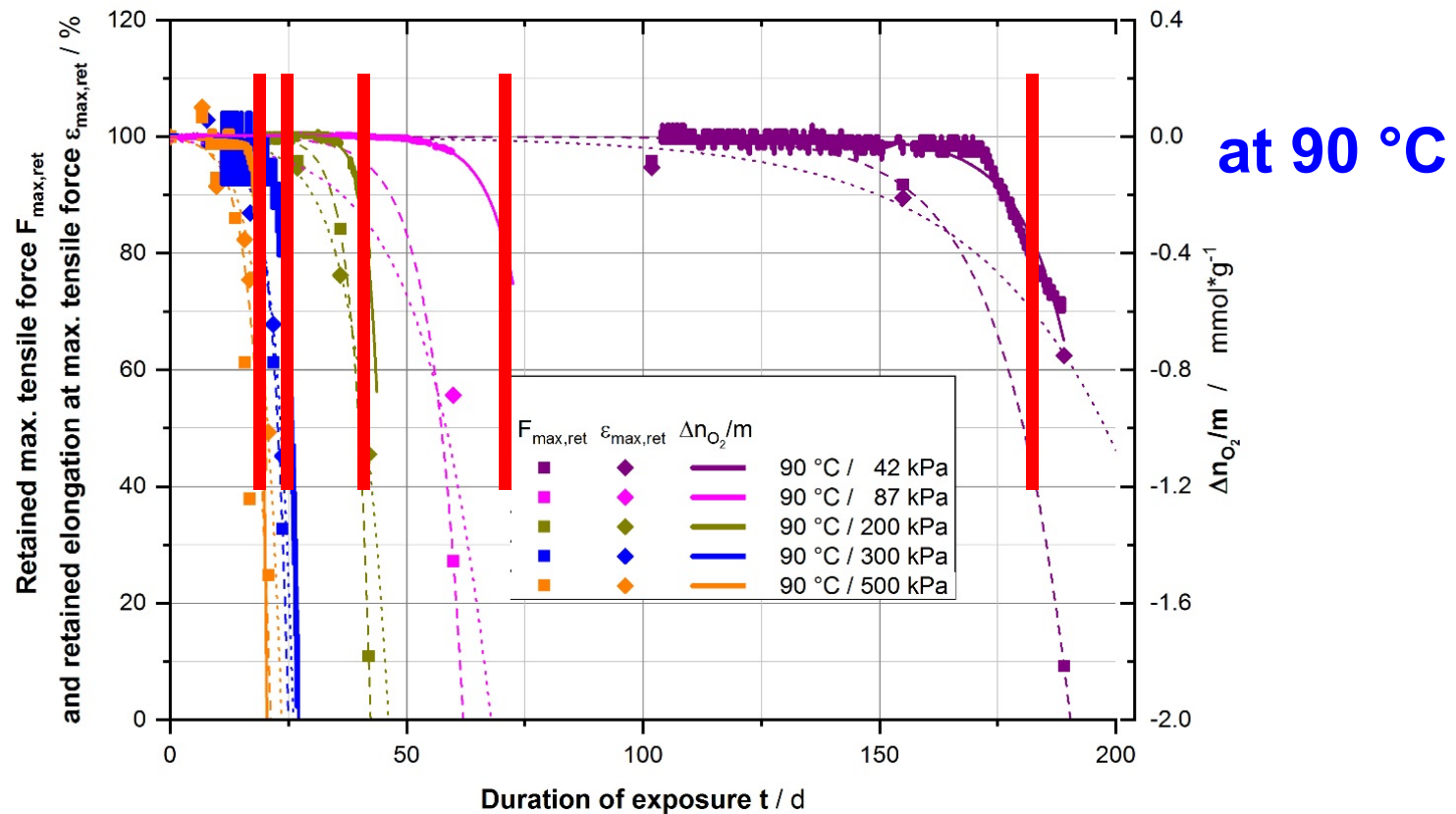
Woven PP-geotextile

Mechanical properties + oxygen consumption



Woven PP-geotextile

Mechanical properties + oxygen consumption

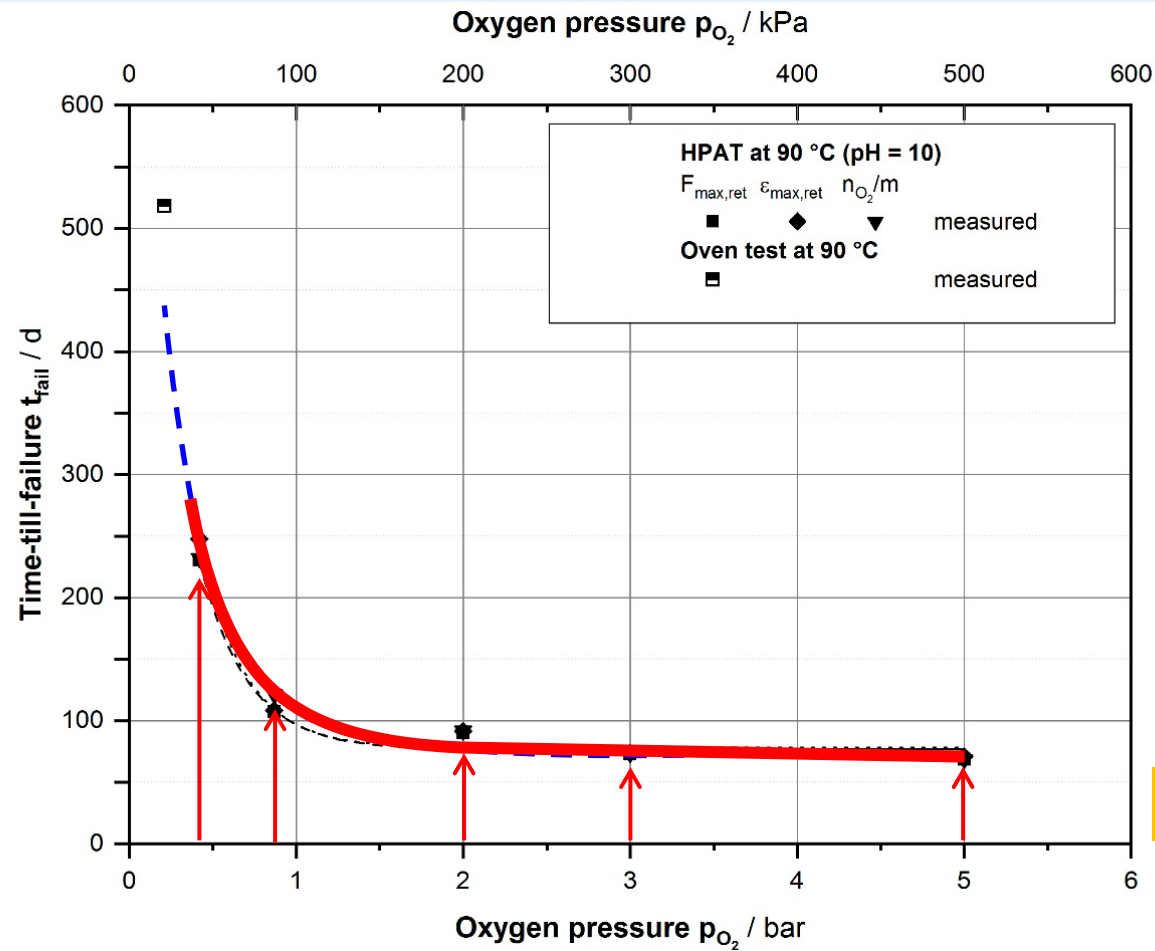


Hausmann et al. (2019).

Oxidative lifetime prediction of a polypropylene woven geotextile by applying high temperature and moderately increased oxygen pressure. (offered for publication to Geotextiles & Geomembranes)

Woven PP-geotextile

Extrapolation regarding O₂-pressure



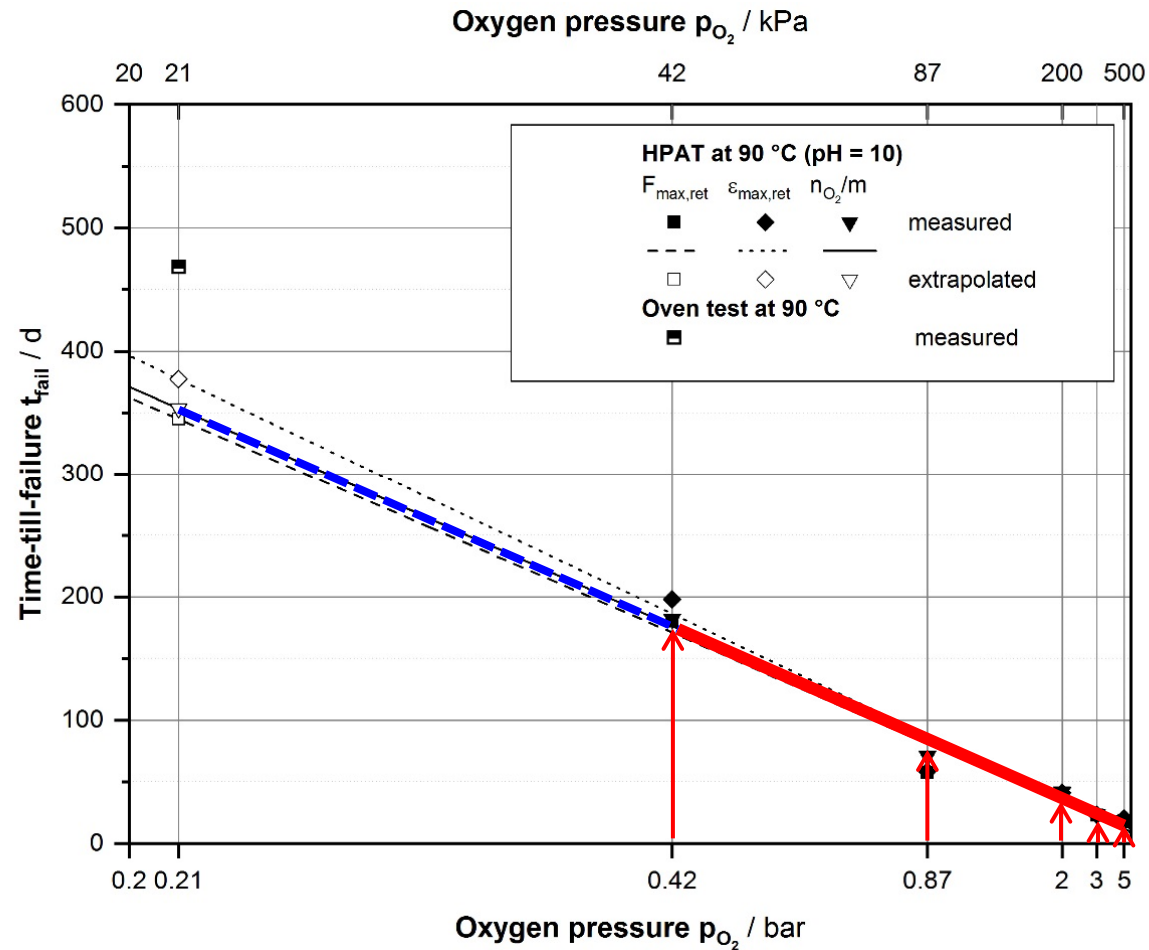
at 90 °C

Linear scale

Woven PP-geotextile



Extrapolation regarding O₂-pressure



at 90 °C

Log scale

Modified Arrhenius models by Schröder et al. (2008)

Model I:

$$1/t_{50\%} = A \cdot \exp\left(\frac{B + C \cdot p_{O_2}}{T}\right)$$

Schröder, H., Böhning, M., Munz, M. (2008).

A new method for testing and evaluating the long-time resistance of oxidation of polyolefinic products, *Polymers and Polymer Composites* 16 (1), pp. 71 – 79.

Model II:

$$1/t_{50\%} = A \cdot \left(\frac{p_{O_2}}{1 + D \cdot p_{O_2}}\right) \cdot \exp\left(\frac{B}{T}\right)$$

Model III:

$$1/t_{50\%} = A \cdot \left(\frac{p_{O_2}}{1 + D \cdot p_{O_2}}\right) \cdot \exp\left(\frac{B + C \cdot p_{O_2}}{T}\right)$$

$t_{50\%}$: half-life period, T: temperature, p_{O_2} : oxygen pressure, A, B, C, D: constants

SKZ-model by Hausmann et al. (2019)

The following Eq. 9 refers to Schröder's Modell II which merely is a multiplication of both previously mentioned relationships on temperature and pressure with the restriction that oxidation is not limited by diffusion.

$$t_{\text{fail}} = \alpha'' \cdot \left(\frac{1 + \beta \cdot p_{\text{O}_2}}{p_{\text{O}_2}} \right) \cdot \exp \left(-\frac{E_A}{R \cdot T} \right) \quad (9)$$

α'' : fit parameter based on Arrhenius equation and α' (cf. Eq. 5), E_A : activation energy, R : universal gas constant, β : fit parameter (cf. Eq. 5)

Hausmann et al. (2019).

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3D-Extrapolation

regarding T and c(O₂) to service conditions

Activation Energy E_A

$$E_A = 84 - 93 \text{ kJ/mol}$$

and

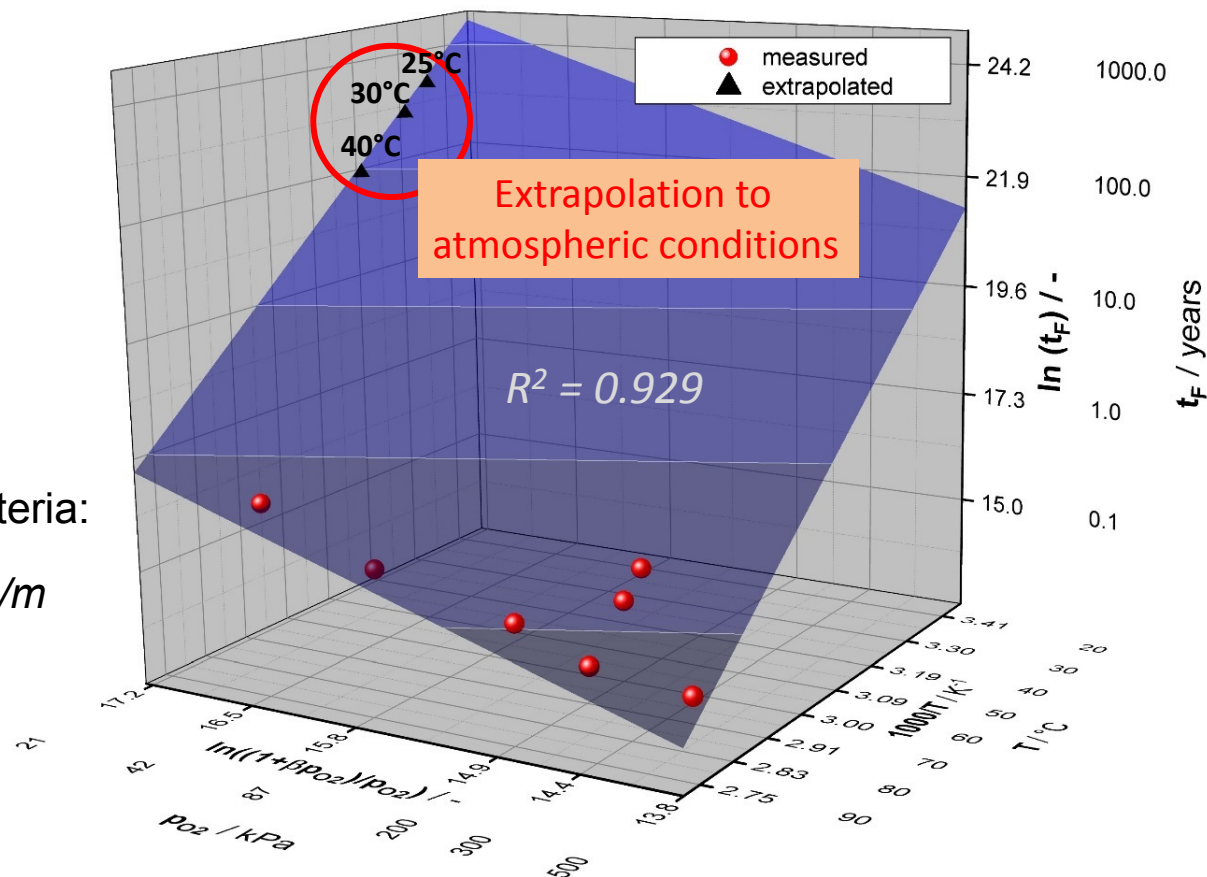
Service Life t

at atmospheric pressure

$$t = 100 - \sim 1000 \text{ years}$$

depend on the chosen failure criteria:

$$F_{max,res} \mid \epsilon_{max,res} \mid p(O_2) \mid n(O_2)/m$$



Service life

at atmospheric O₂-partial pressure and various temperatures

Temperature °C	Service life based on failure criteria ... years		
	$F_{\max, \text{res}} = 50\%$	$\epsilon_{\max, \text{res}} = 50\%$	$\Delta n_{\text{O}_2}/m = -0.4$ mmol/g
20	863	1091	1502
25	483	602	795
30	275	339	430
35	160	195	237
40	94	114	133

Hausmann et al. (2019).

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Summary

- Time-till-failure at **oven testing** @ 90 °C: ~ 500 d
- Time-till-failure at **HPAT** @ 90 °C: < 50 d (*depending on O₂-pressure applied*)
- Time of abrupt **oxygen pressure** drop (= *significant consumption of O₂*)
correlates with time-till-failure based on **mechanical properties**.
- “Temperature dependency” of HPAT results: **Arrhenius typical**
- “Pressure dependency” of HPAT results: **Double logarithmic**
- Activation energy $E_A = 85 - 93$ kJ/mol
- **Service life estimation** based on HPAT results: ~200 years @ e.g. 35 °C

Questions are welcome.
Thank you for your interest.



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Marine Aging of Polymers