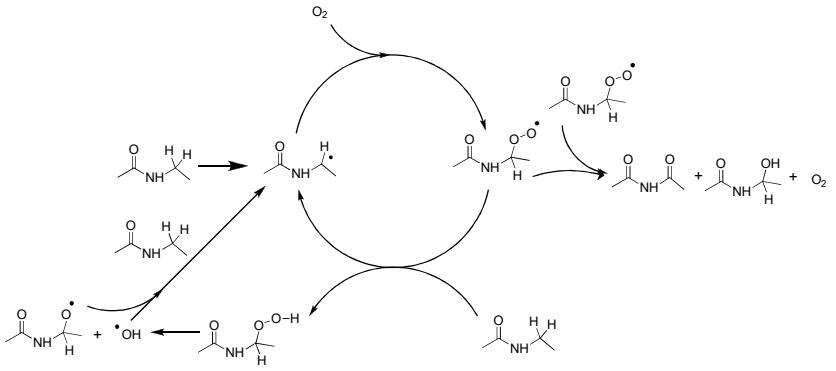
The unexpected importance of humidity on the thermo-oxidative and photo-oxidative degradation of polyamides

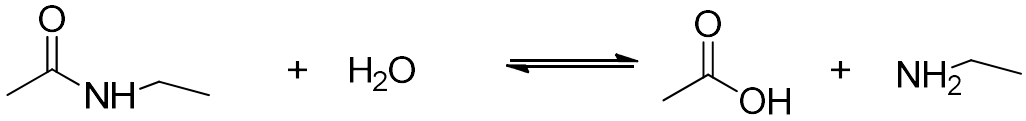
Pieter Gijsman

Introduction

- It is well known that Polyamides degrade as a result of oxidation



- Polyamides can degrade due to hydrolysis with water from the environment



- Environments contains oxygen as well as water
  - Is there an influence water on the life time of polyamides? If so is this a result of hydrolysis?
    - Thermo-oxidative
    - Weathering

Influence humidity on:

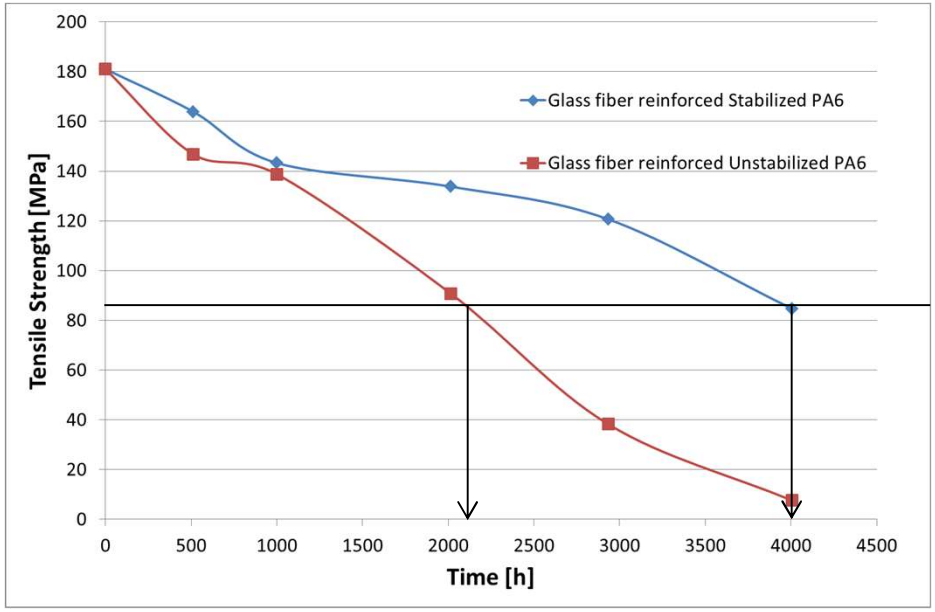
1. Thermo-oxidative ageing of polyamide 6

- Influence of humidity on the decrease in mechanical properties
- Change in molecular weight in humid conditions
- Oxygen uptake at dry and humid conditions
  - Experimental
  - Oxygen uptake:
    - » Dry conditions (100-180°C)
    - » Humid conditions (50-85°C)
  - Conclusions

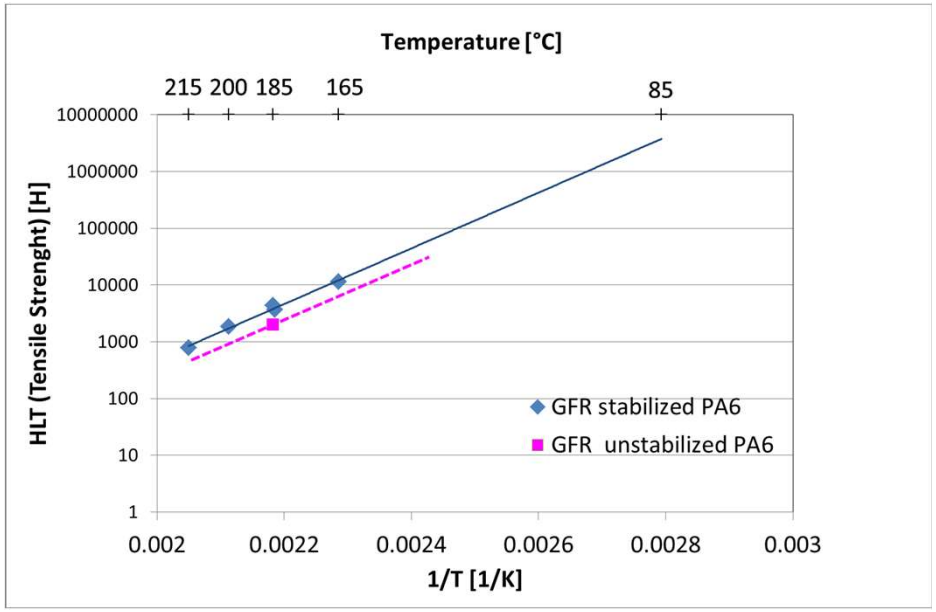
2. Weathering of polyamide 6

Oven-ageing of PA6 in dry air

Tensile strength GFR PA6 as a function of oven-ageing time at 185°C



Arrhenius plot GFR PA6



Expected HLT at 85°C of GFR PA6 in dry air >> 100 years

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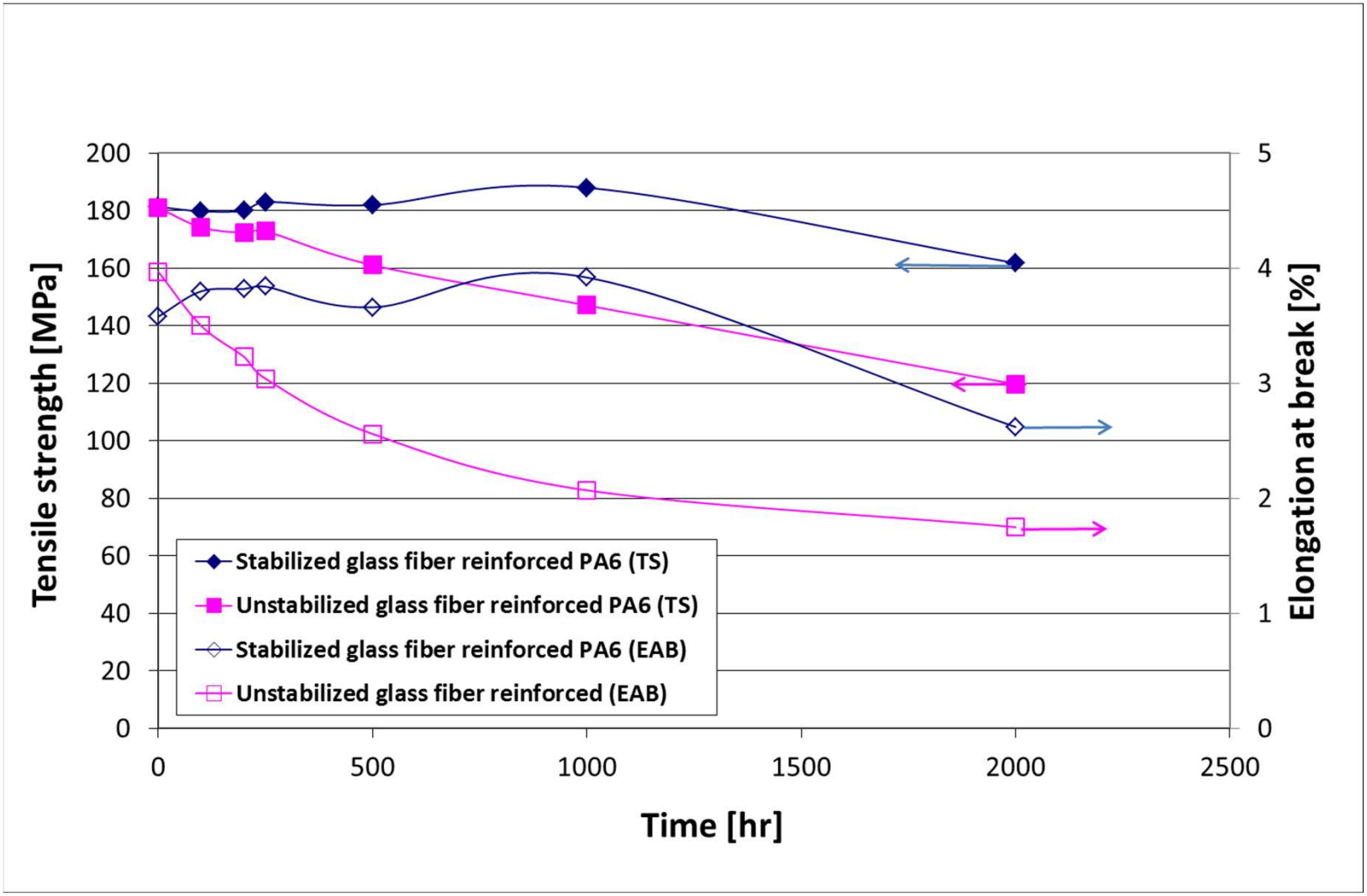
Ageing of glass fiber reinforced stabilized and unstabilized polyamide 6 at 85°C / 90% RH



Humidity has a tremendous influence on the stability of GFR PA6

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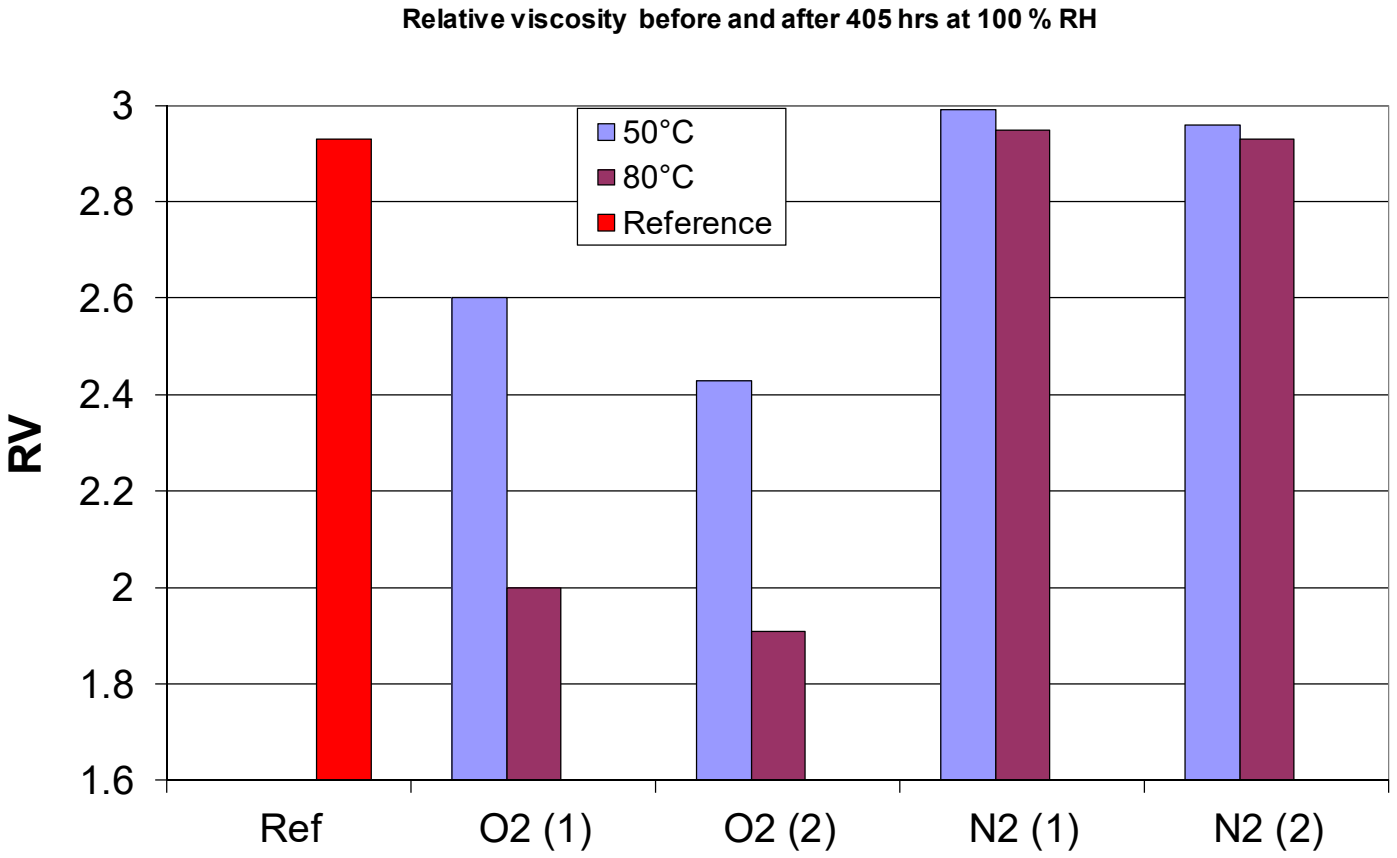
Experimental (Oxygen uptake)

- Polymer studied polyamide 6
  - 50 µm thick 6 films
  - 3 mm thick pars
- Vessels filled with PA6, oxygen or nitrogen and liquid water.
  - PA6 films were brought in the vessel so that there was no contact with the liquid water and closed.
- These vessels were heated to 50 - 85°C and after releasing a bit pressure closed.
- In this way nitrogen and oxygen atmospheres with a relative humidity of 100% were created.
- Pressure was recorded as a function of ageing time from which the oxygen uptake was calculated
- Changes in molecular weight were determined using Relative Viscosity measurements with Formic Acid as solvent

Degradation of 50µm thick PA6 films at 85°C/ 100% RH (closed System)



No change in molecular weight (Relative Viscosity, RV) in wet nitrogen. Considerable decrease in molecular weight in wet oxygen.

Hydrolysis is during thermo-oxidative degradation not important!!

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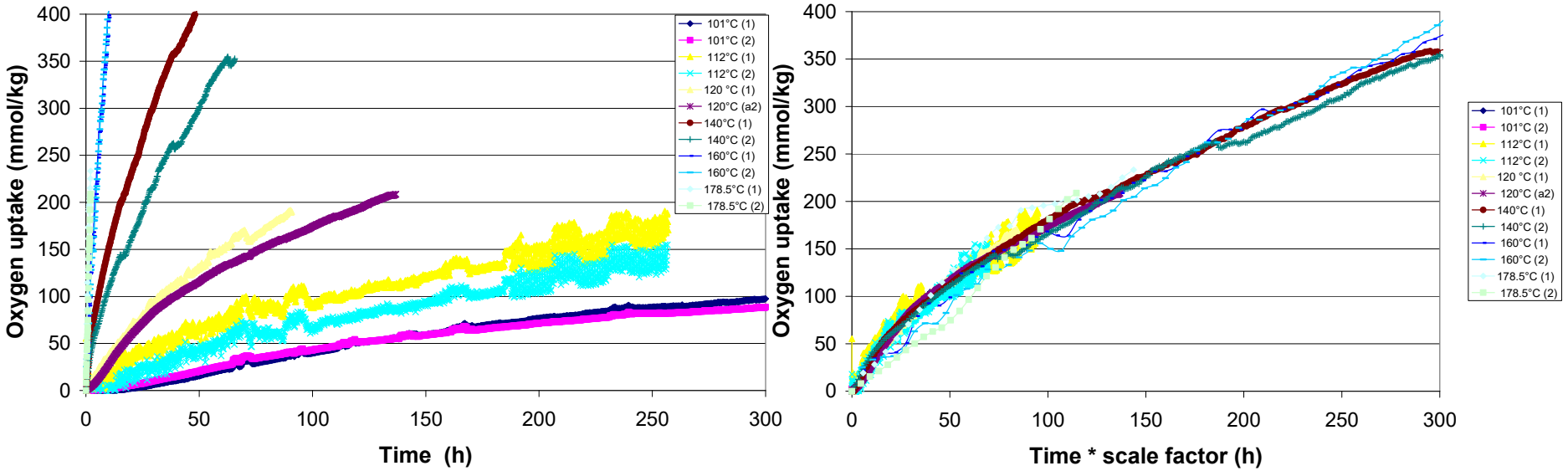
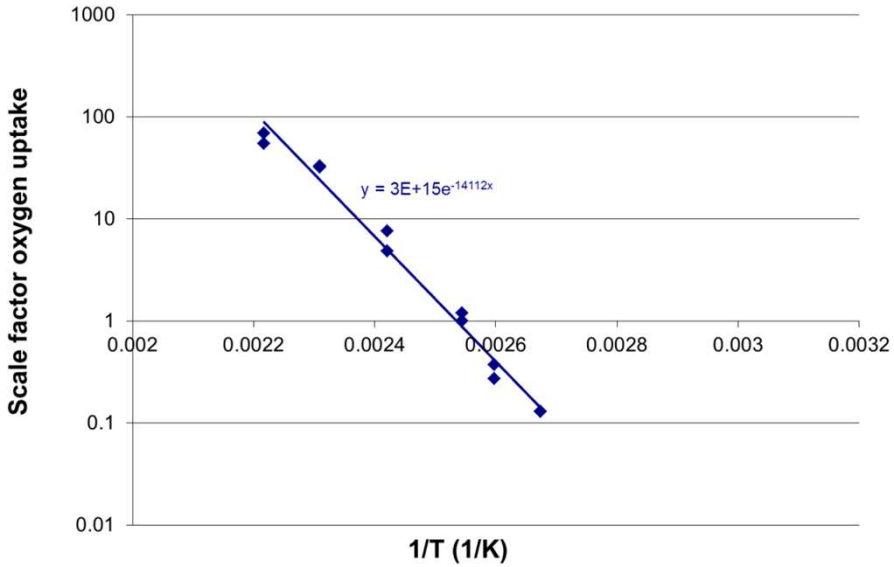
Influence of temperature (100 – 180°C) on oxygen uptake rate of PA6 films (Dry)





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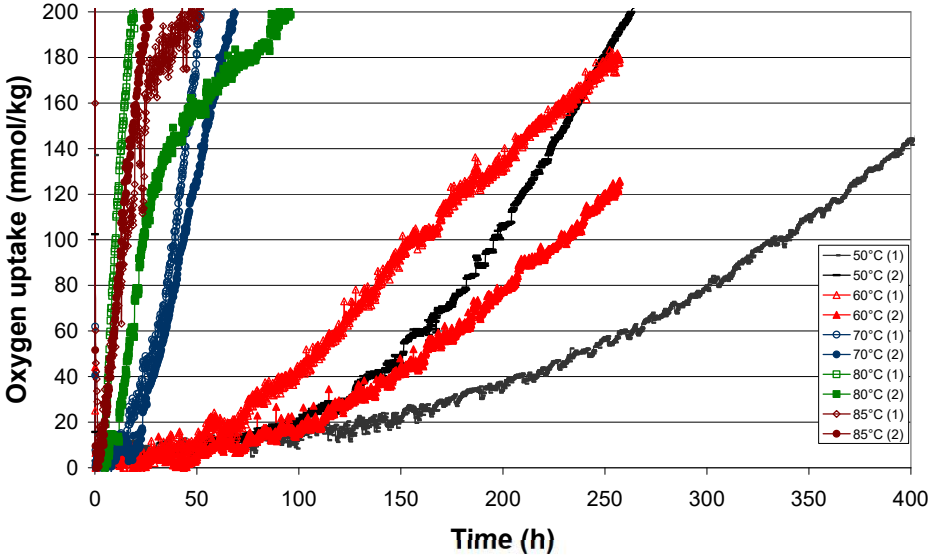
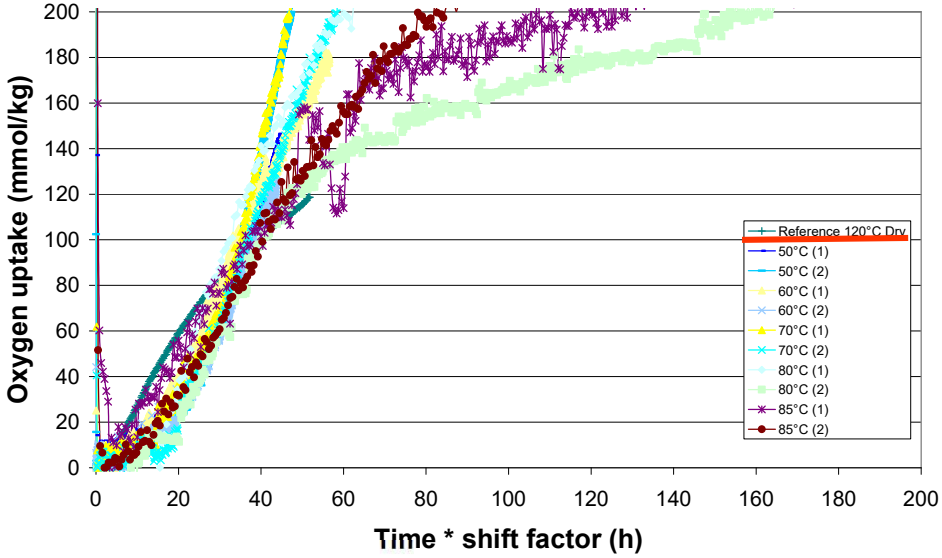
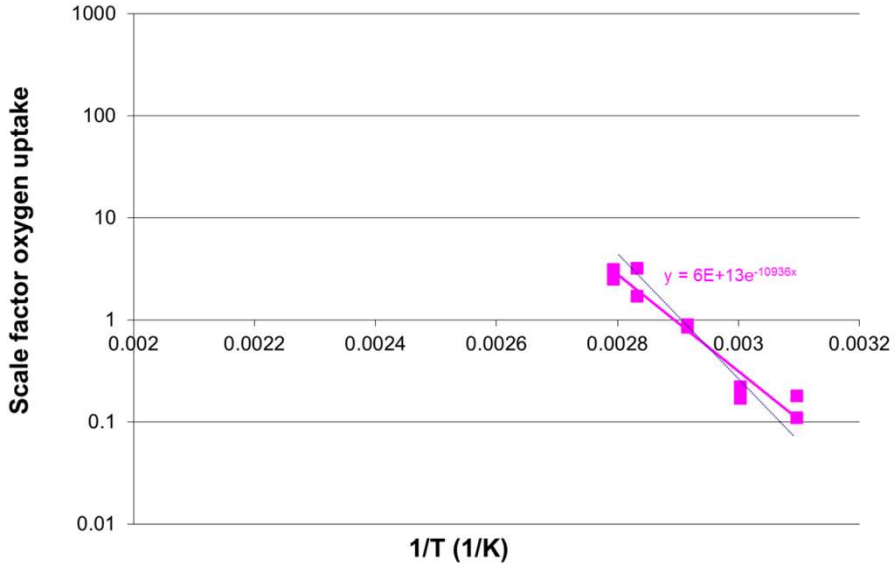
Influence of temperature (50 – 85°C) on oxygen uptake rate of PA6 films (Humid)







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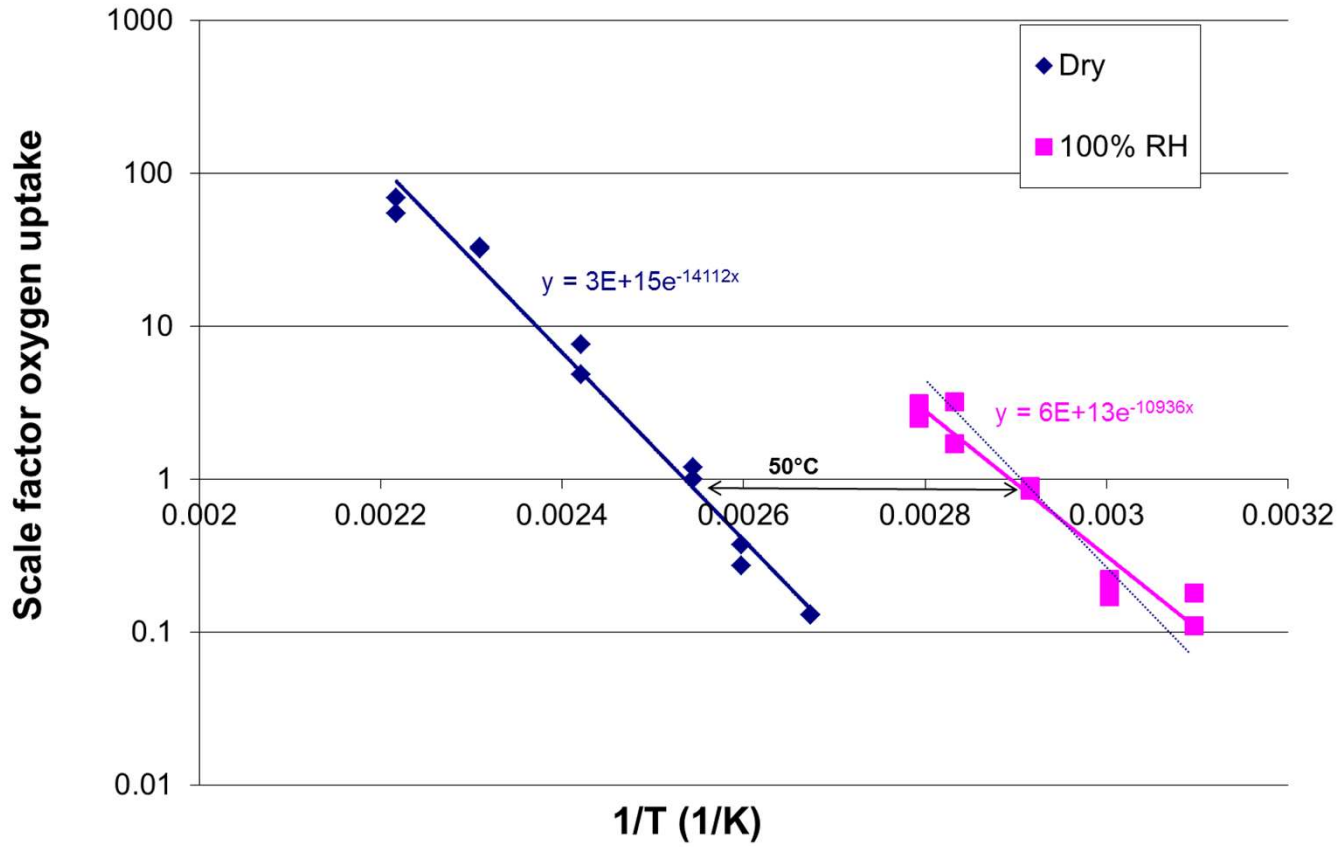
Arrhenius plot oxygen uptake polyamide 6 in dry and wet (100% RH) oxygen



Humidity cause a large increase in oxidation rate

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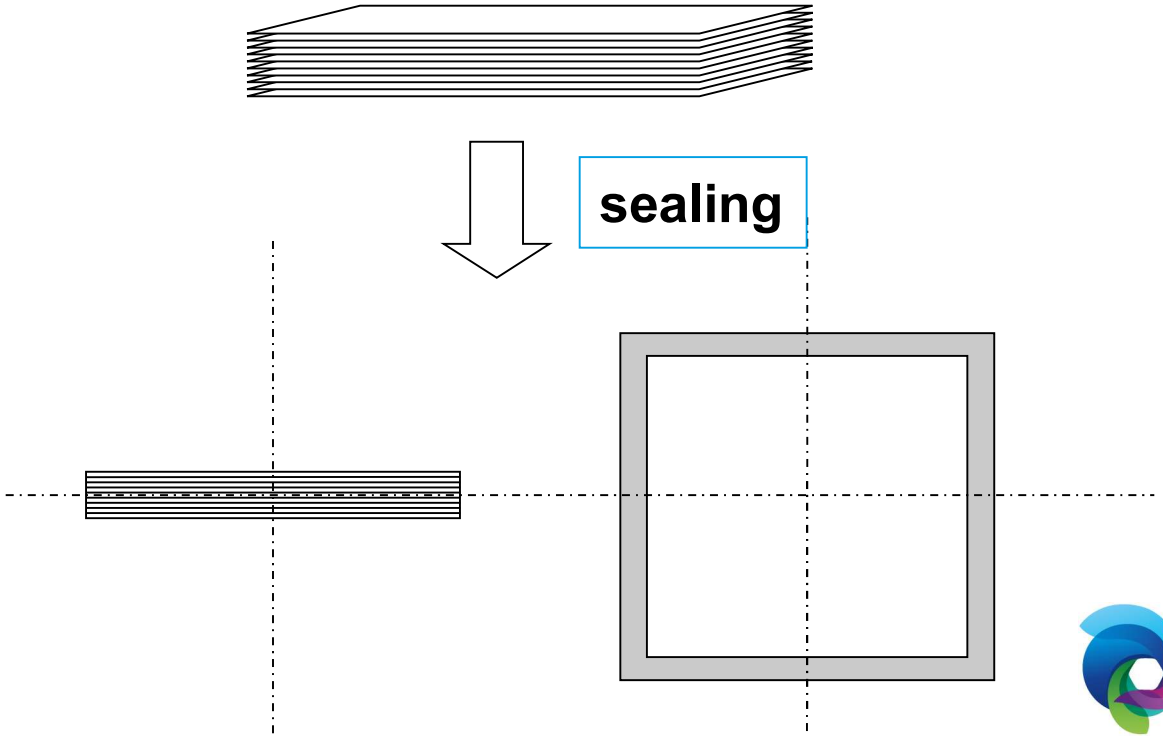
Oxygen diffusion limitation in the oxidation of Polyamide 6 (Dry)

Unstabilized sandwiches:

1. Preparation of sample (sandwiches);
2. Ageing of sandwiches at different temperatures (dry)
3. Measurement of profiles (individual layers)



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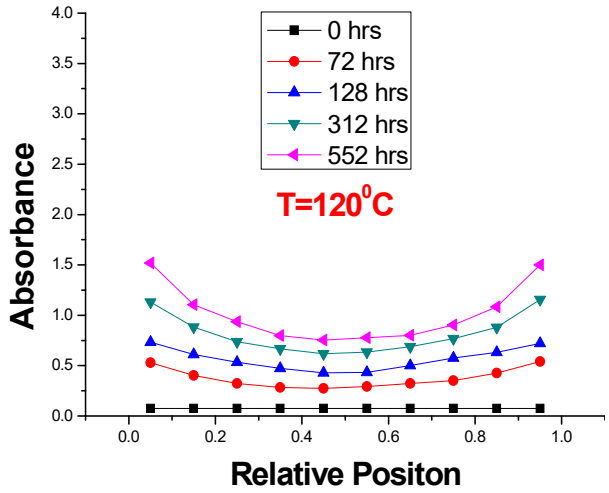
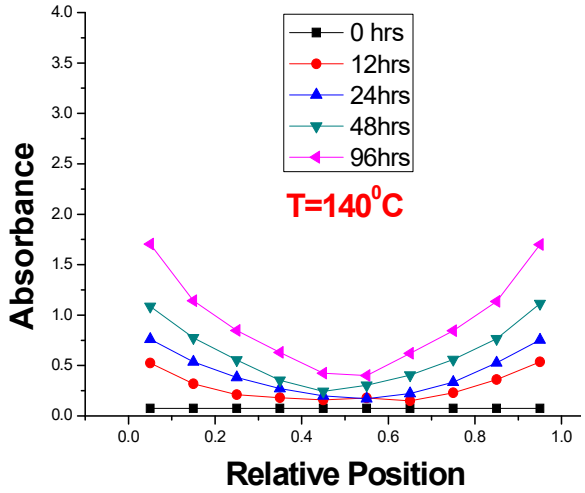
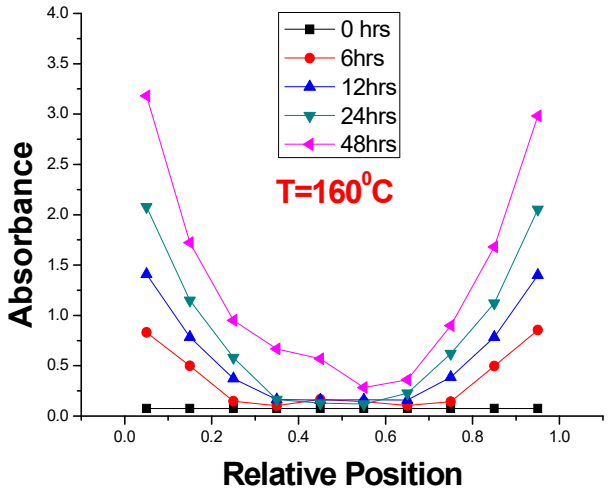
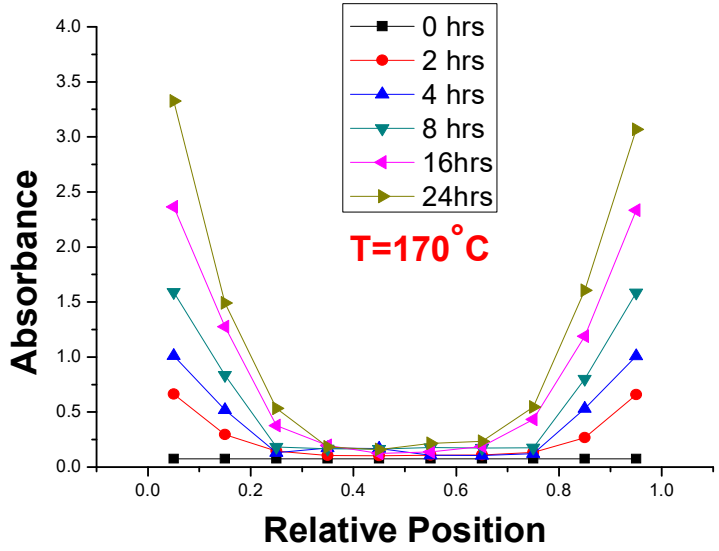
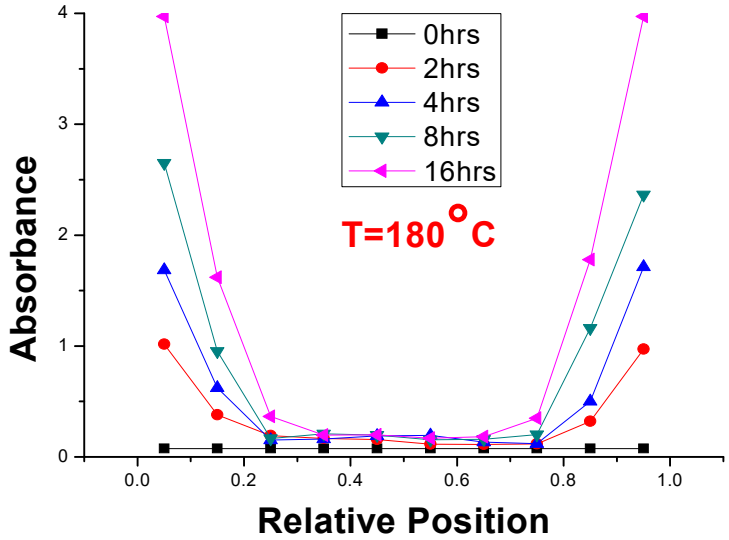
Oxygen diffusion limitation in PA6 (dry)











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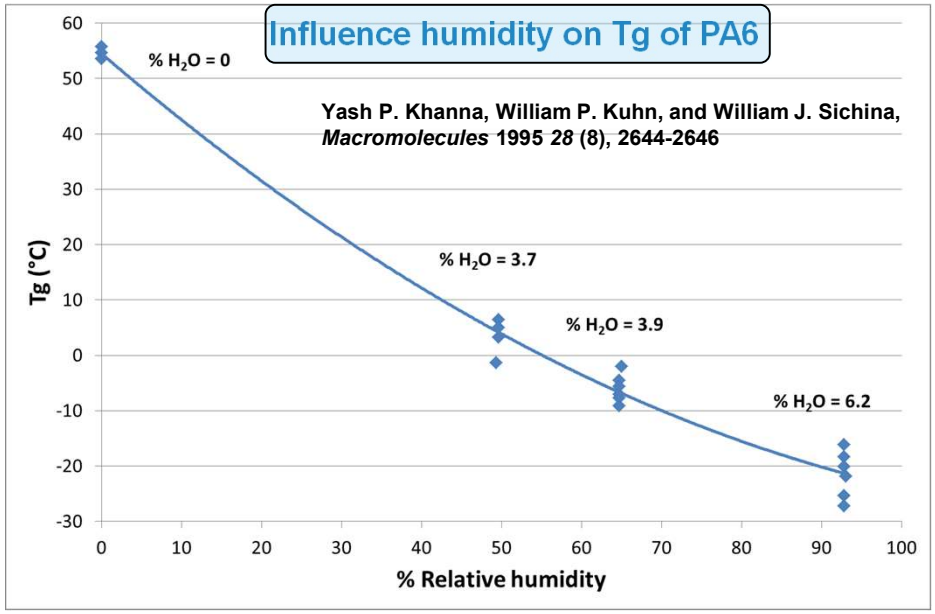
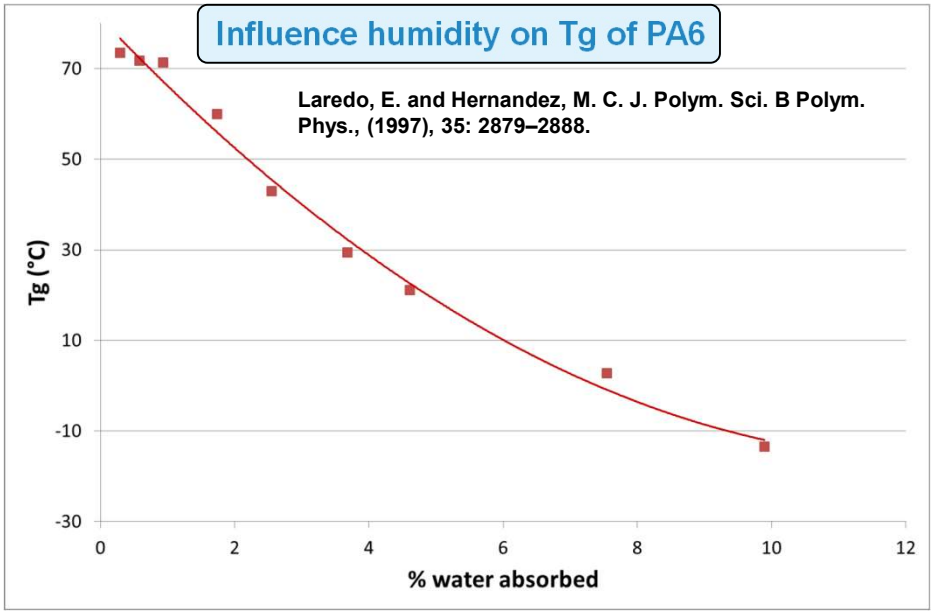
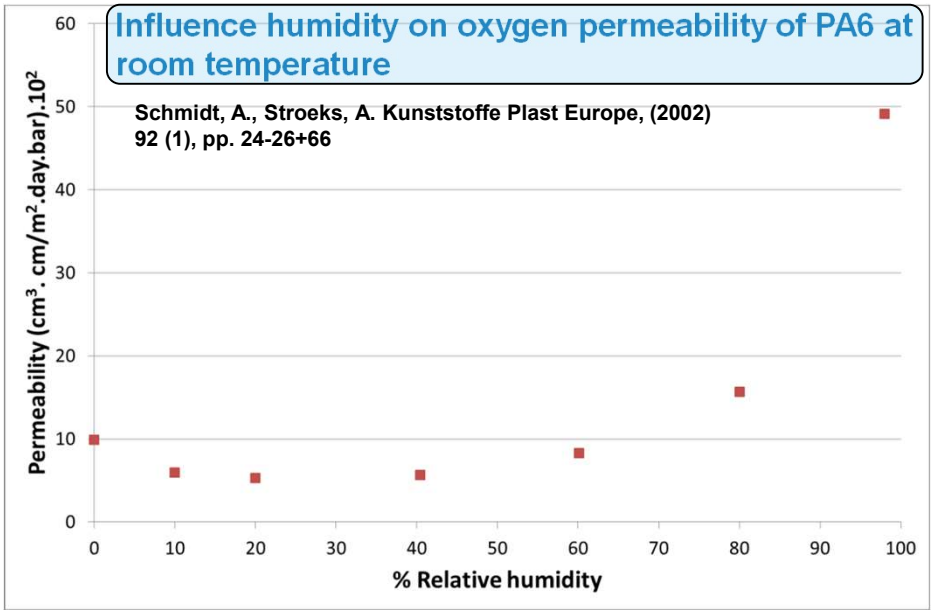
Influence humidity on Tg and Oxygen Permeability of PA6







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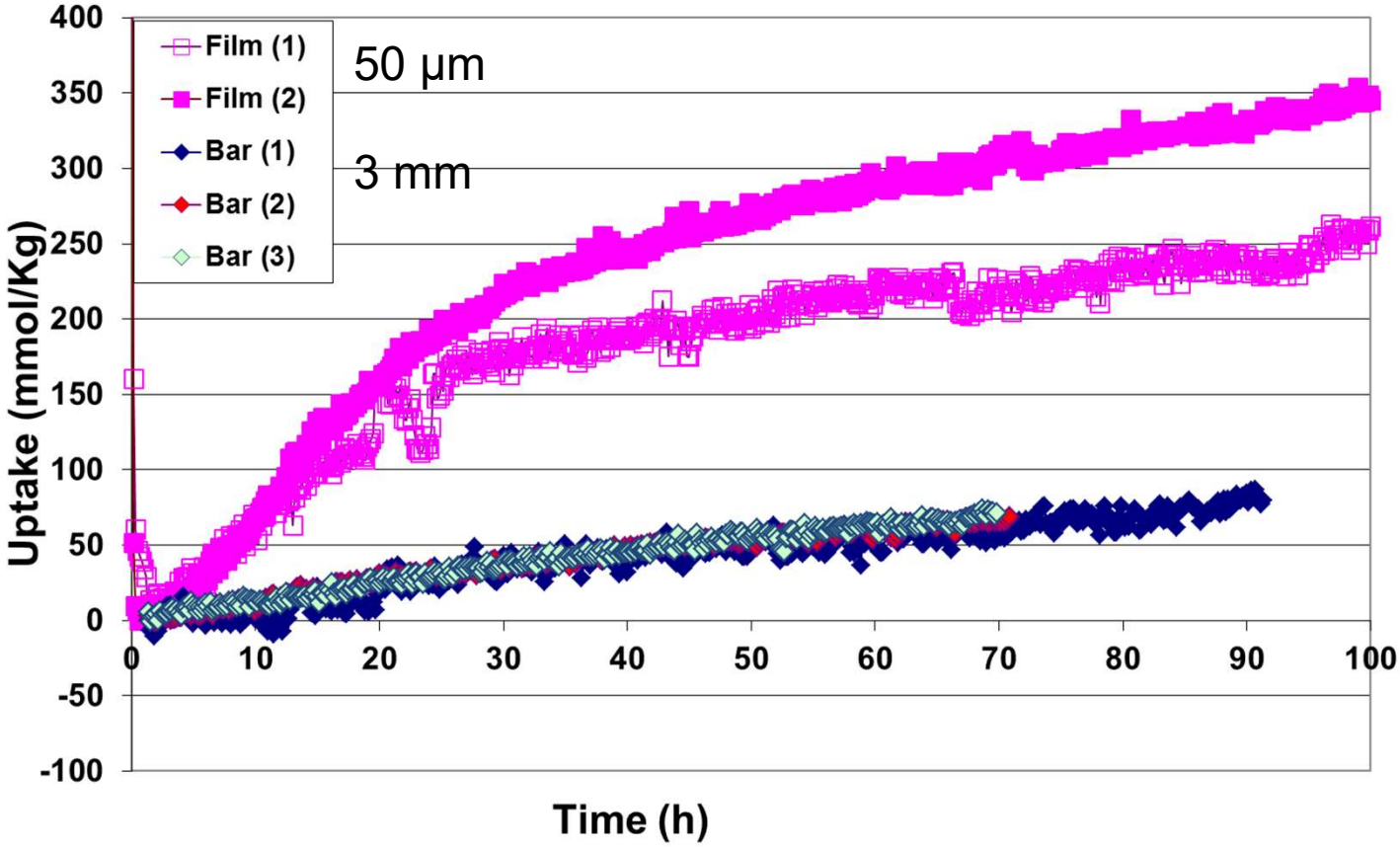
Influence thickness on oxygen uptake in humid oxygen (85°C and 100%RH)



In humid conditions oxidation still oxygen diffusion limited

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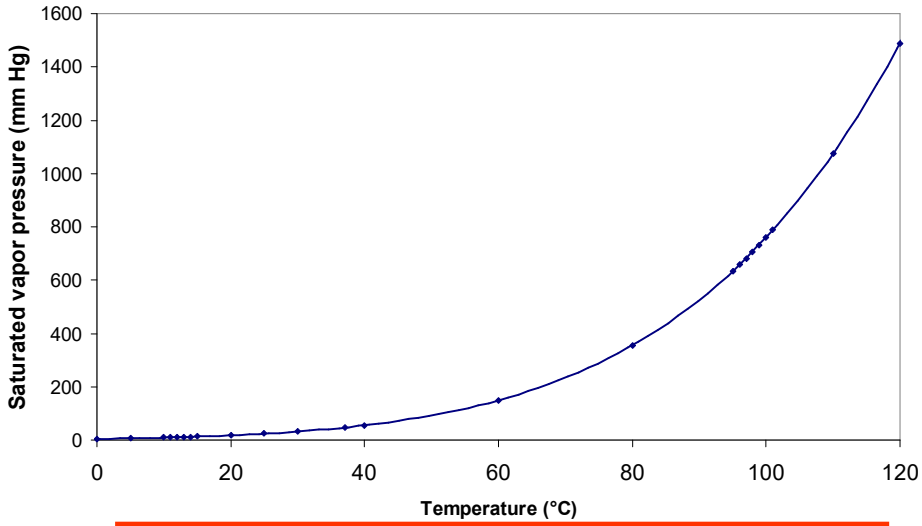
Conclusions influence humidity on the thermo-oxidative degradation of PA6

- The decrease of the stability of polyamide during oven-ageing is not due to hydrolysis, but due to of an increase in oxidation rate.
- Water absorption lead to a decrease in Tg causing an increase in oxygen diffusion rate, nevertheless the oxidation is still oxygen diffusion limited (influence thickness)
- The higher oxidation rate in humid conditions is probably due to an increase in chain mobility.

Relevance humidity on life time determination

- Application dependent:
  - Ageing at environmental conditions moisture is not important as combinations between high humidity and high temperatures hardly exists.



Increase in temperature from 31 to 80 ºC leads to a decrease in relative humidity from 80% to less than 10%

  - For applications in contact with water it can be important

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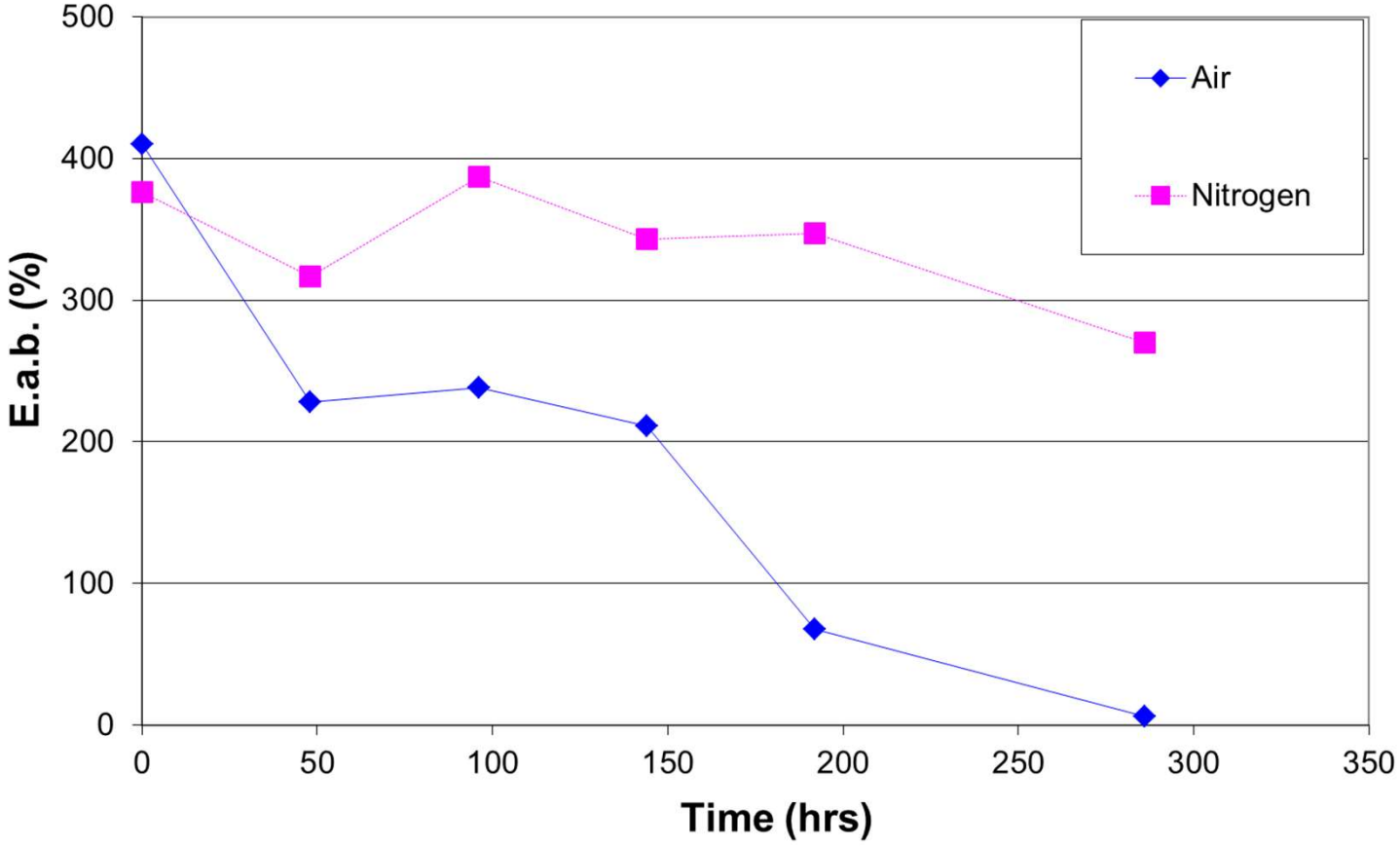
2. Influence of humidity on the weathering of polyamide 6

- Photo-degradation mechanism
- Influence humidity/rain on accelerated weathering
- Correlation between accelerated and outdoor weathering
- Influence humidity on the photo-degradation rate
- Influence humidity on the weathering of glass fiber reinforced PA6
- Conclusions

Mechanism of photo-degradation of PA6

Accelerated weathering of PA6 in air and in nitrogen (dry)



Gijsman P, Diepens M, Photolysis and Photooxidation in Engineering Plastics
Polymer Degradation and Performance. January 1, 2009, 287-306

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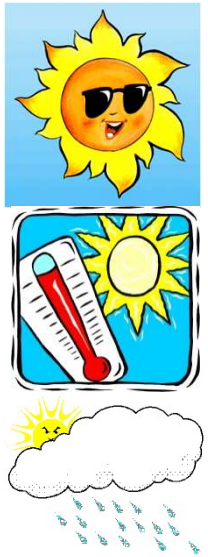
Weathering is due to a complex combination of factors

- **Solar radiation**
  - **Degradation mainly due to UV part of the radiation**
- **Temperature**
  - **Air temperature ≠ Sample temperature**
- **Moisture**
  - **Rain,**
  - **Humidity**
- **Other factors**
  - **Acid rain, other pollutants**
  - **Mechanical stresses, abrasion**
  - **Biological attack (mold, mildew, bird droppings)**
  - **……**



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Accelerated weathering methods used:

- Direct (accelerated) weathering

	Florida simulating condition (Dry/Wet)	Arizona simulating condition (Dry)
Accelerated test equipment:	Atlas Weather-Ometer, Ci65A	Atlas Weather-Ometer, C3000
Test standard:	ASTM G 155 (november 2000) (successor of ASTM G26); ISO 4892-2	PV3929 (Volkwagen)
Specification of test conditions:		
Light source:	Xenon light source filtered with inner and outer borosilicate S filters	Xenon light source filtered with inner and outer borosilicate S filters
Black standard temperature:	67 ± 2 °C	90 ± 2 °C
Test chamber temperature:	42-45 °C	50 °C
Radiation intensity:	0.35 ± 0.02 W/m2/nm at 340nm	0.6± 0.02 W/m2/nm at 340nm
Relative humidity (end of dry period):	50 ± 5 %	20 ± 5 %
Dry/wet cycle:	102 min dry/18 min front water spray	None
Light/dark cycle:	Continuous illumination	Continuous illumination

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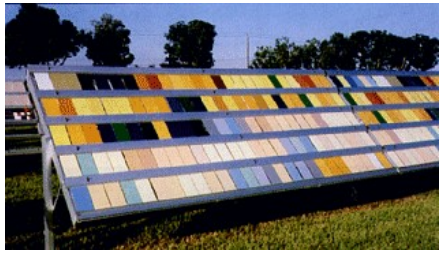
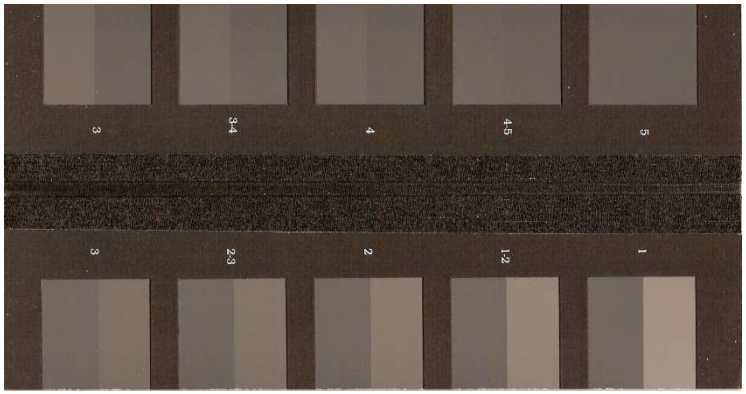
Outdoor weathering

Standard Outdoor Site
South Florida
South France (Bandol)



Accelerated weathering
UVB
UVA
Weather-Ometer

Gray scale evaluation method



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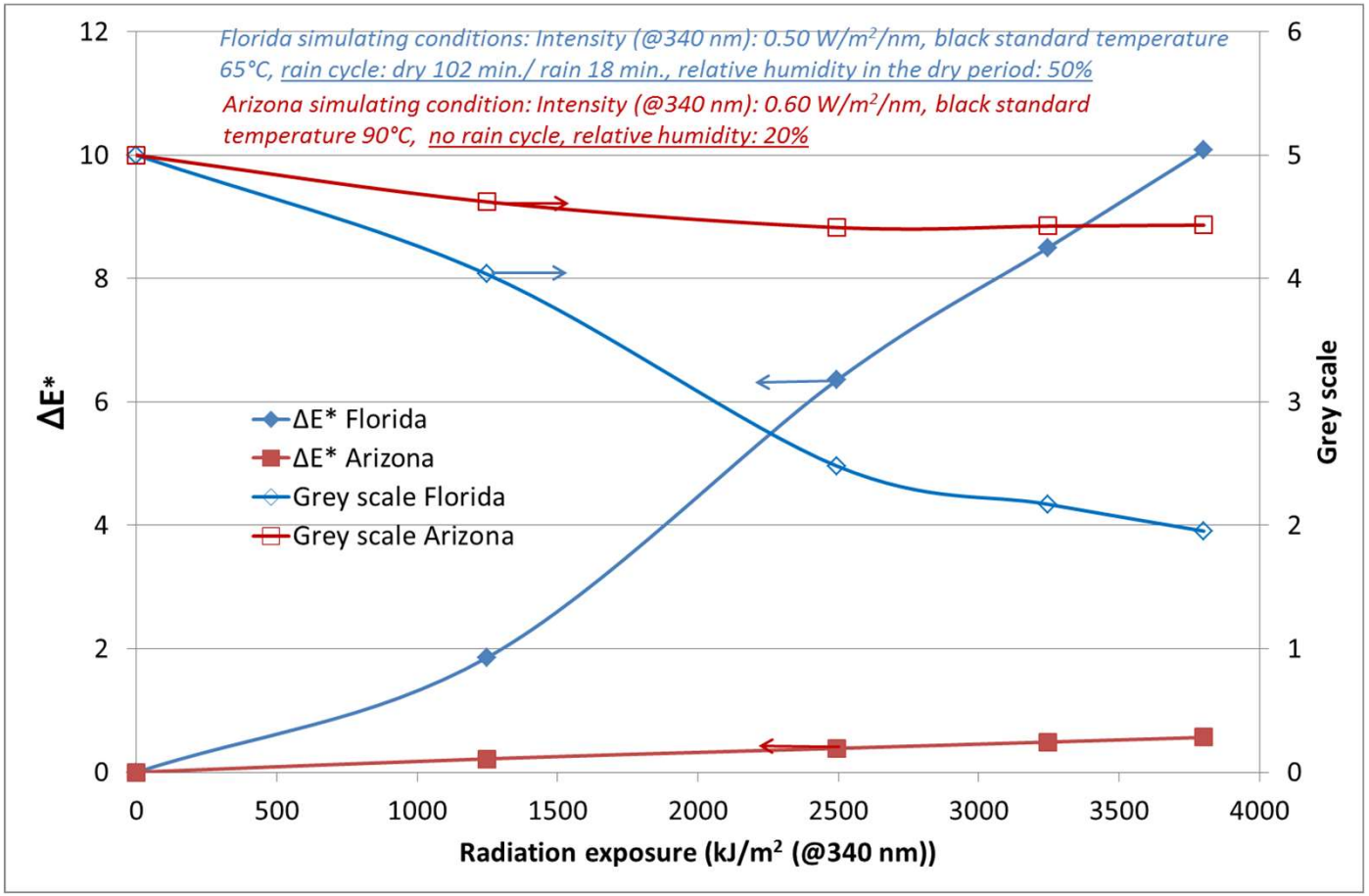
Influence moisture on the accelerated weathering of glass fiber reinforced grey PA6



Moisture has a large influence on the weathering of GFR PA6

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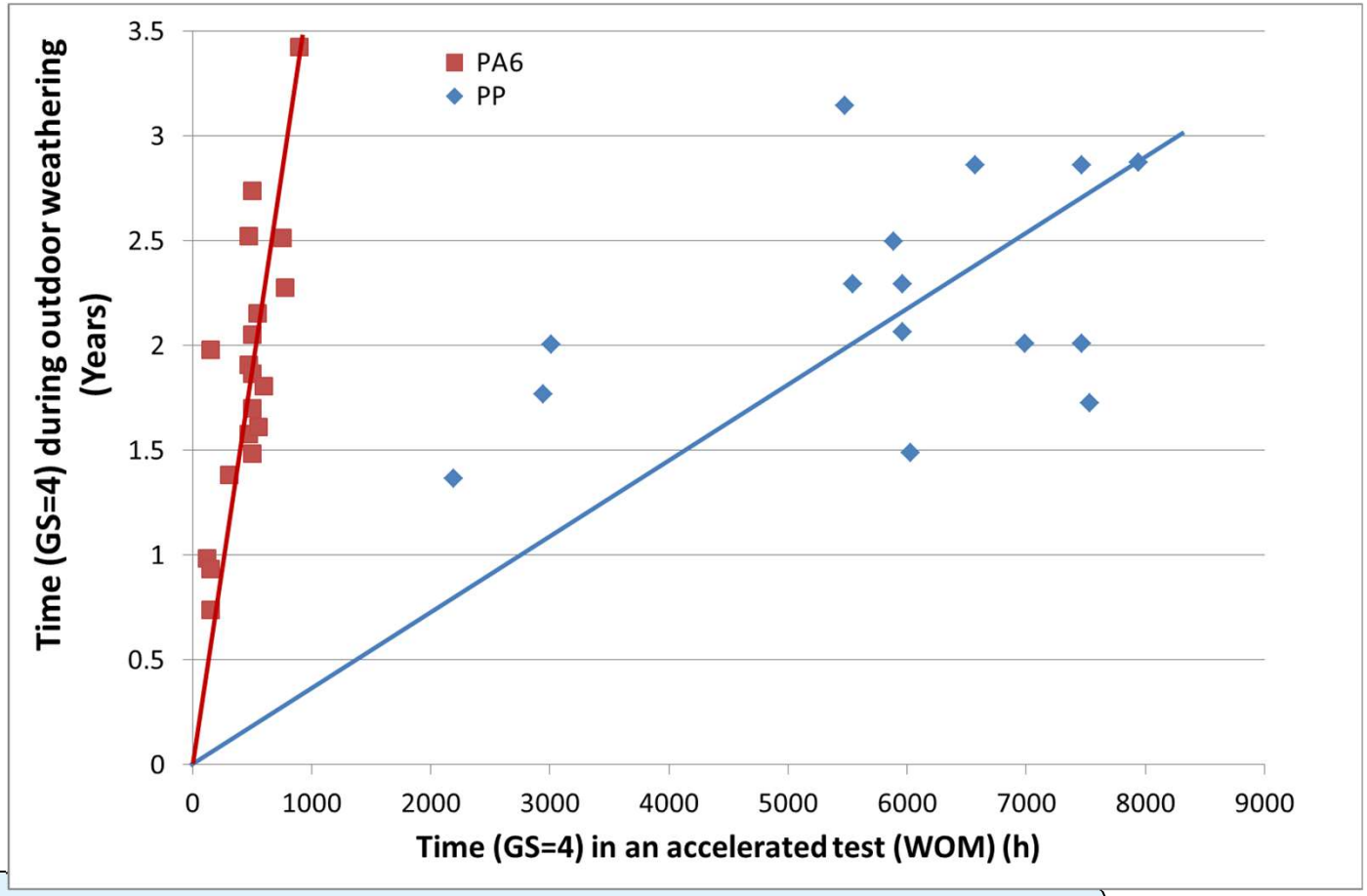
Relation between outdoor (South France) and accelerated weathering (WOM) for grey GFR PA6 and PP



Relation between accelerated and outdoor weathering for PA6 (water absorbing) and PP (non-water absorbing) totally different??

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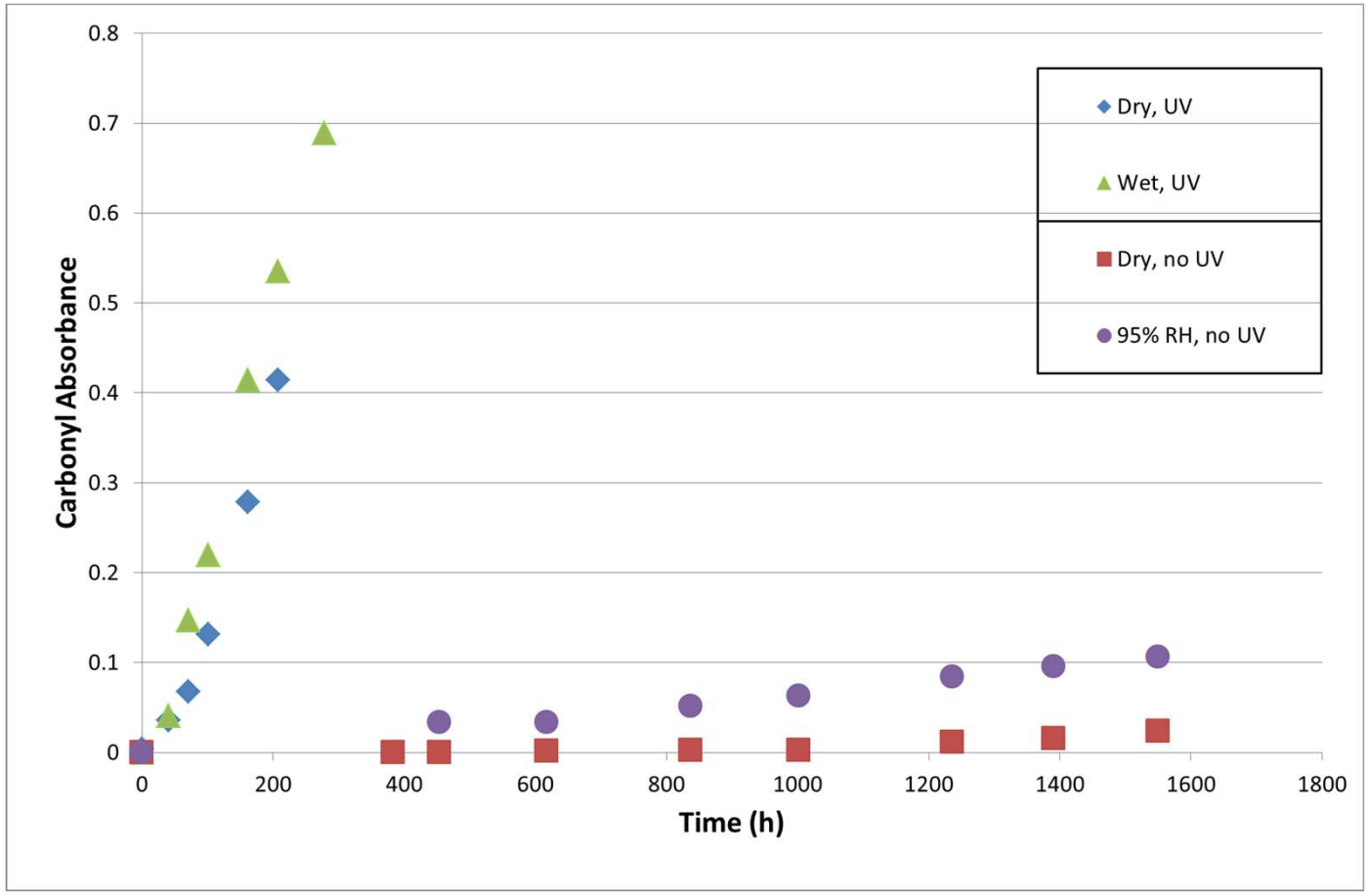
Influence of humidity on the oxidation rate of PA6 films (50µm) during weathering in a Weather-Ometer (ASTM G155) and in air at 64 °C



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Influence environment on weathering of PA6 films
(photolysis, photo-oxidation, hydrolysis)

Relative Viscosity of PA6 films after 637 h accelerated weathering in borosilicate vessels

t = 637 h	[RV in FA 90%]
Reference	3.37
PA6 film Air, wet	1.99
PA6 film Air, dry	1.40
PA6 film N_2, wet	3.27
PA6 film N_2, dry	3.34

Only in the presence of oxygen, the sample degrades.
No real difference between dry and humid conditions.

Photo-oxidation

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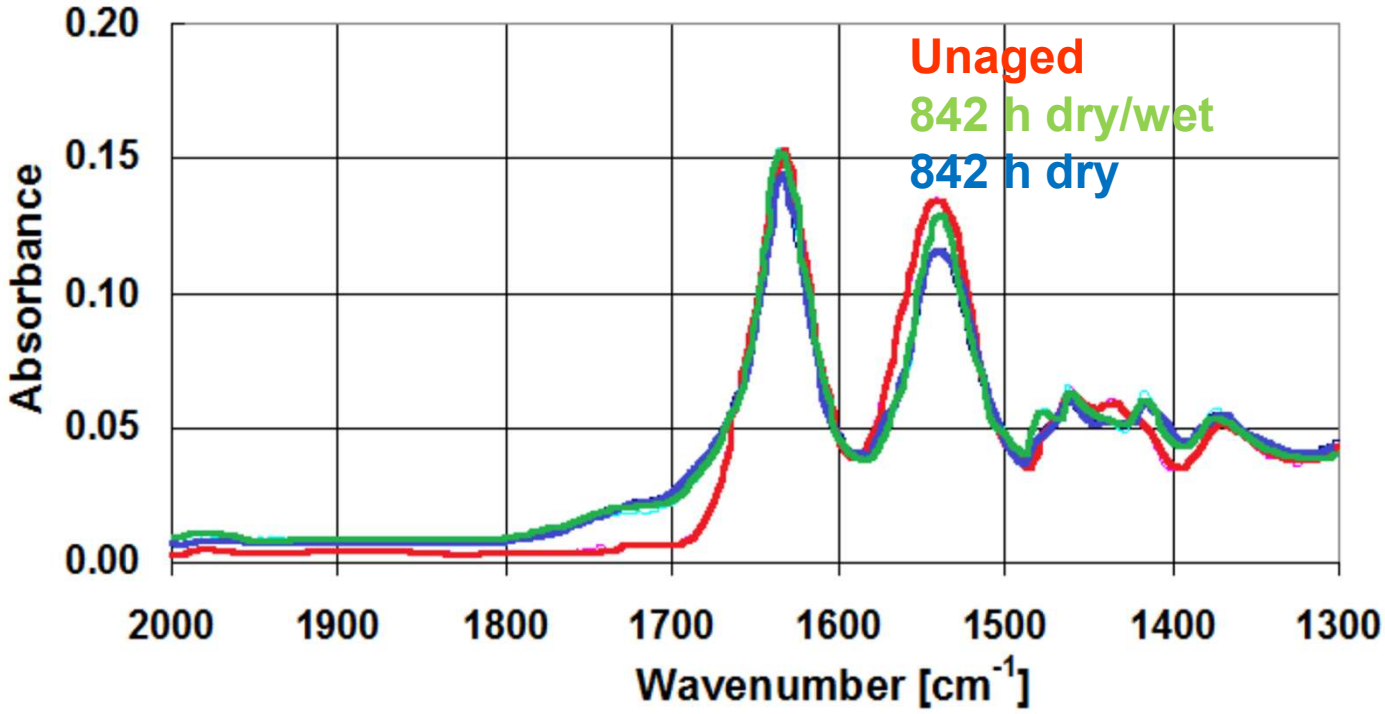
Influence humidity on oxidation rate GFR PA6

weathering in a Weather-Ometer (ASTM G155)



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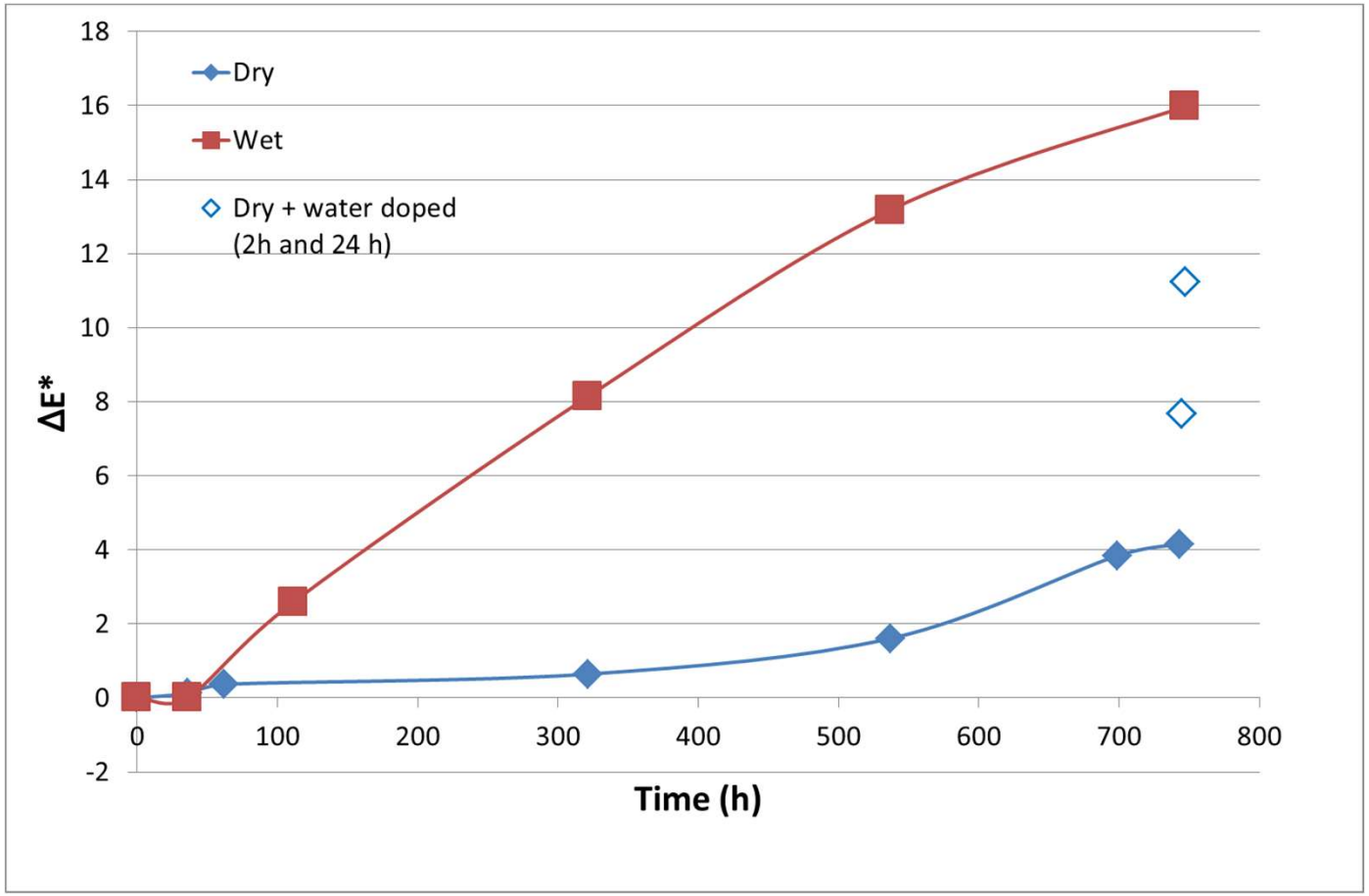
Influence moisture on the accelerated weathering of glass fiber reinforced grey PA6

Influence water treatment after dry accelerated ageing on colour



Water treatment has a large influence on ΔE.

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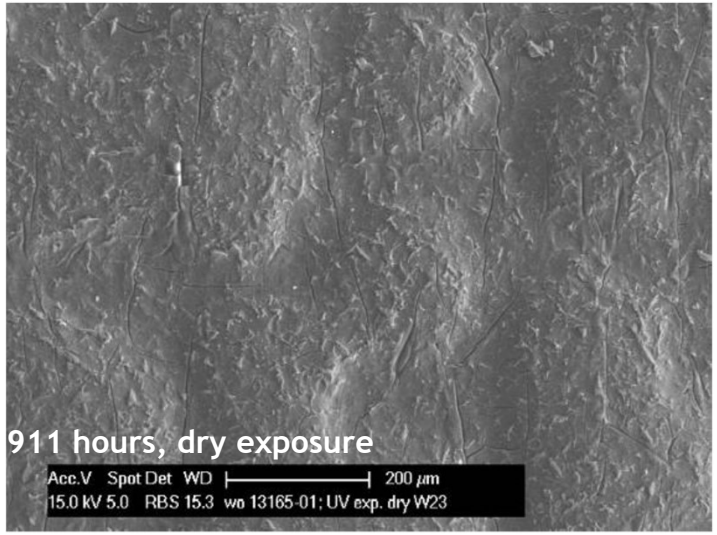
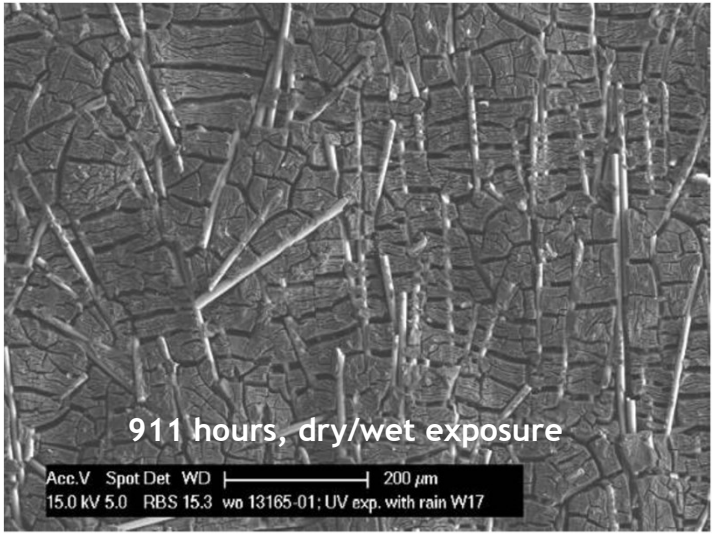
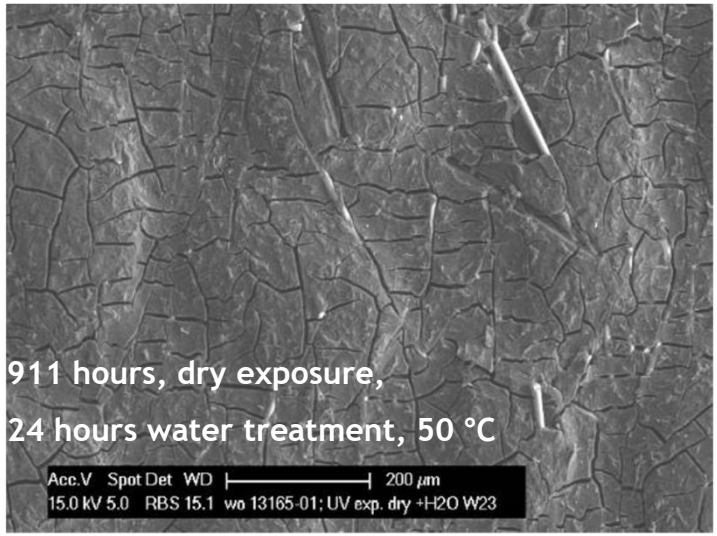
Influence water on the accelerated weathering of glass fiber reinforced grey PA6

Influence water treatment after UV ageing on surface appearance







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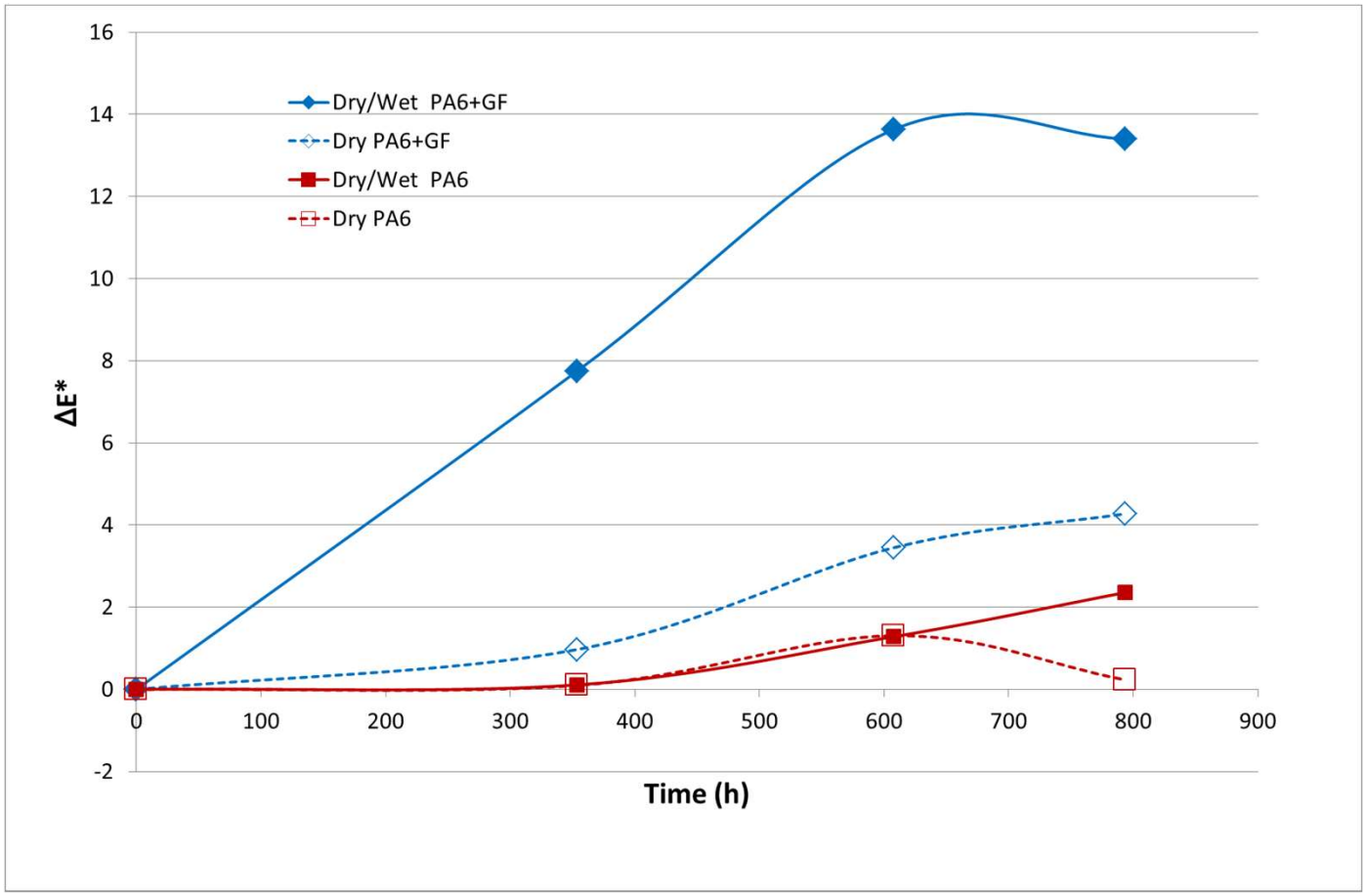
Influence GF reinforcement on the influence of moisture during accelerated weathering of PA6 plaques



Influence moisture in the presence of GF much larger

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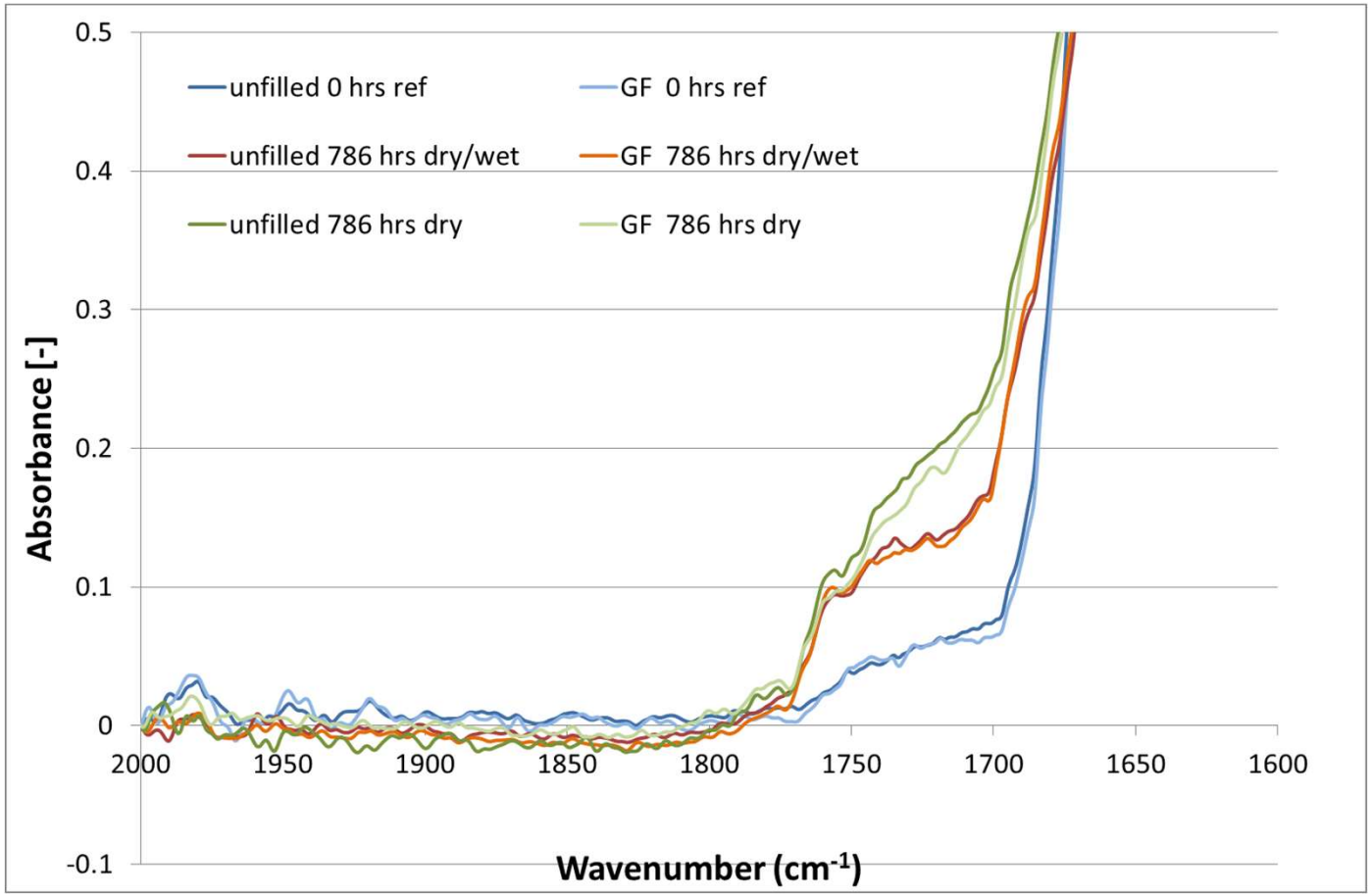
Influence of moisture on the oxidation of PA6 during accelerated weathering



GF have no influence on the oxidation rate of PA6
Samples irradiated under dry conditions show highest Carbonyl absorption

Results M. Diepens

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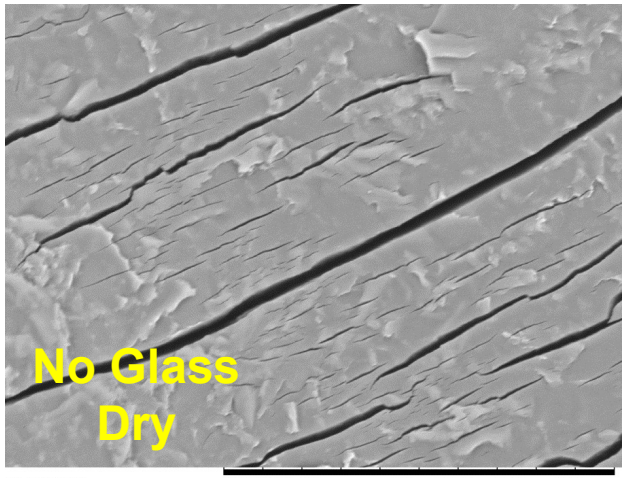
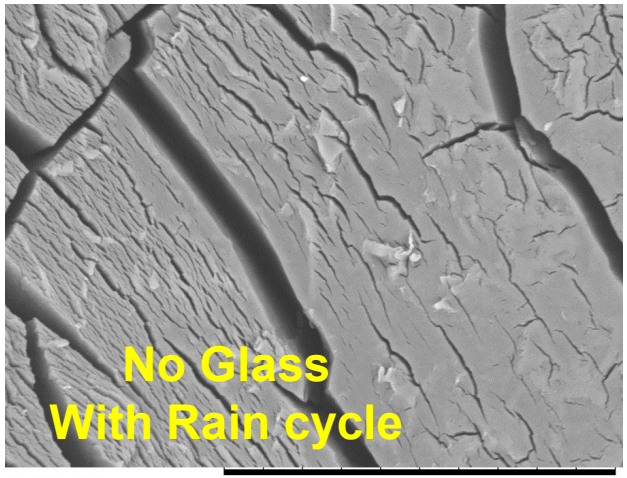
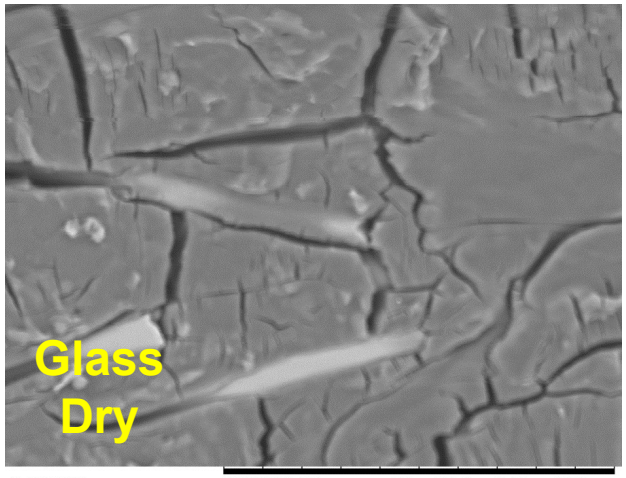
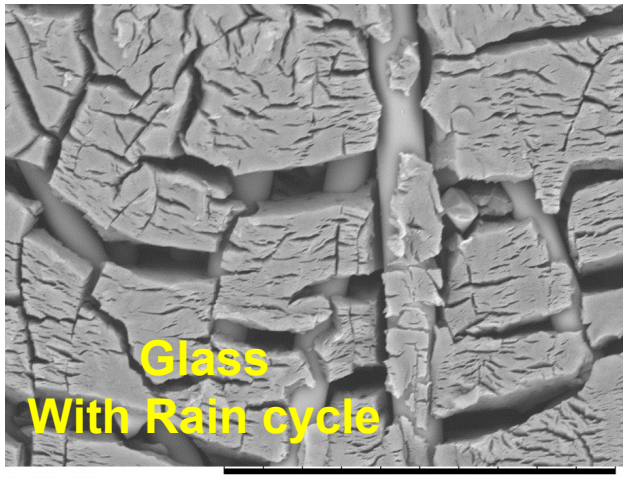
Influence GF reinforcement on the influence of moisture during weathering of PA6

SEM pictures after 768 h weathering









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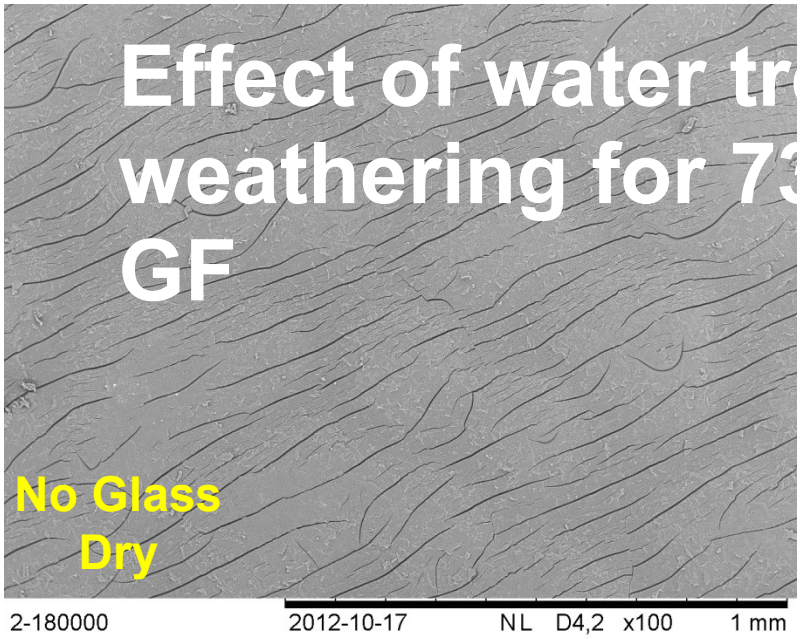
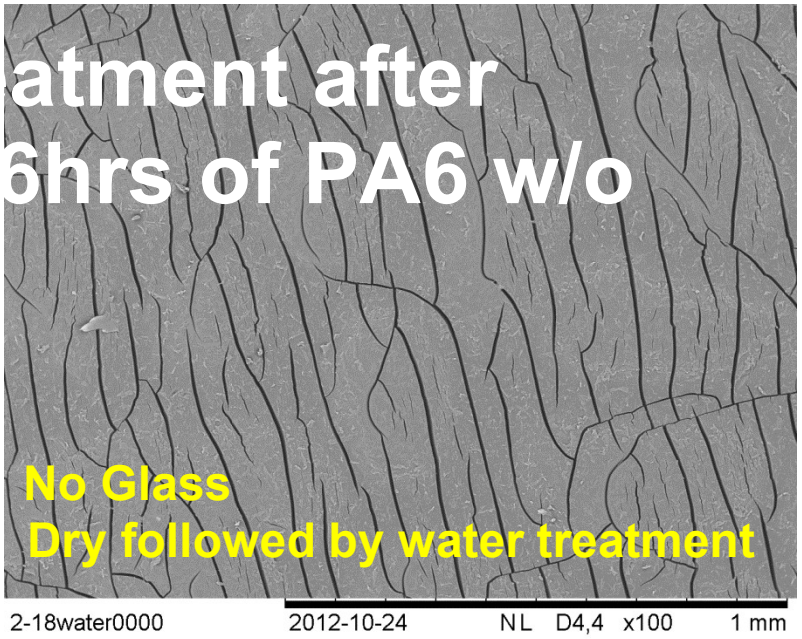
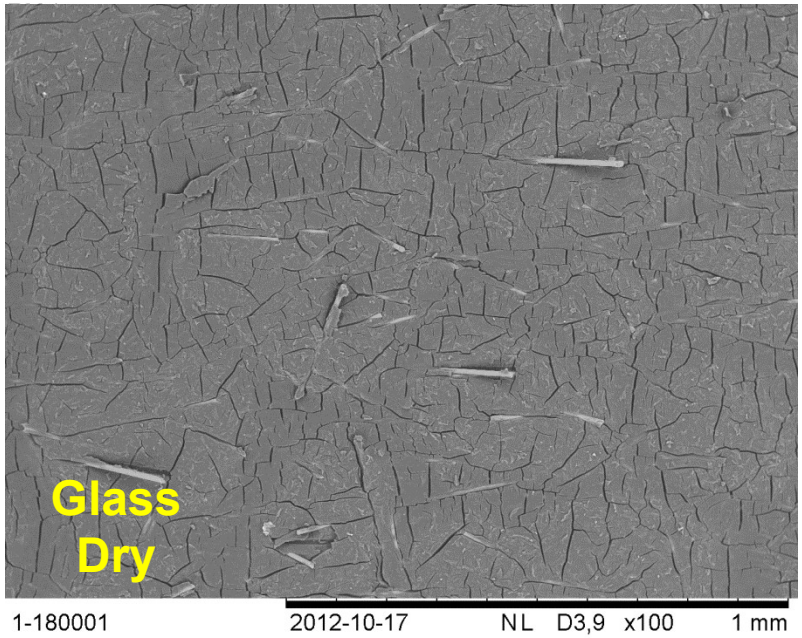
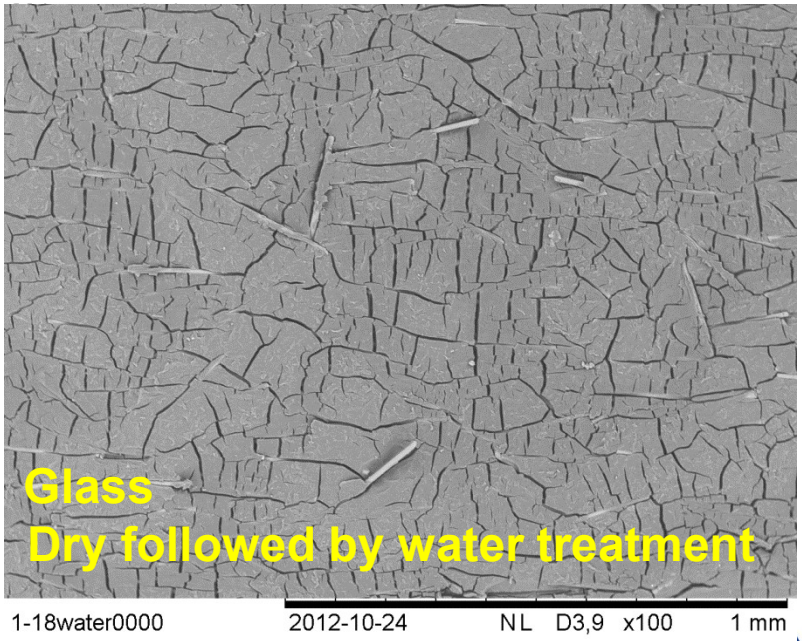
Effect of water treatment after weathering for 736hrs of PA6 w/o GF





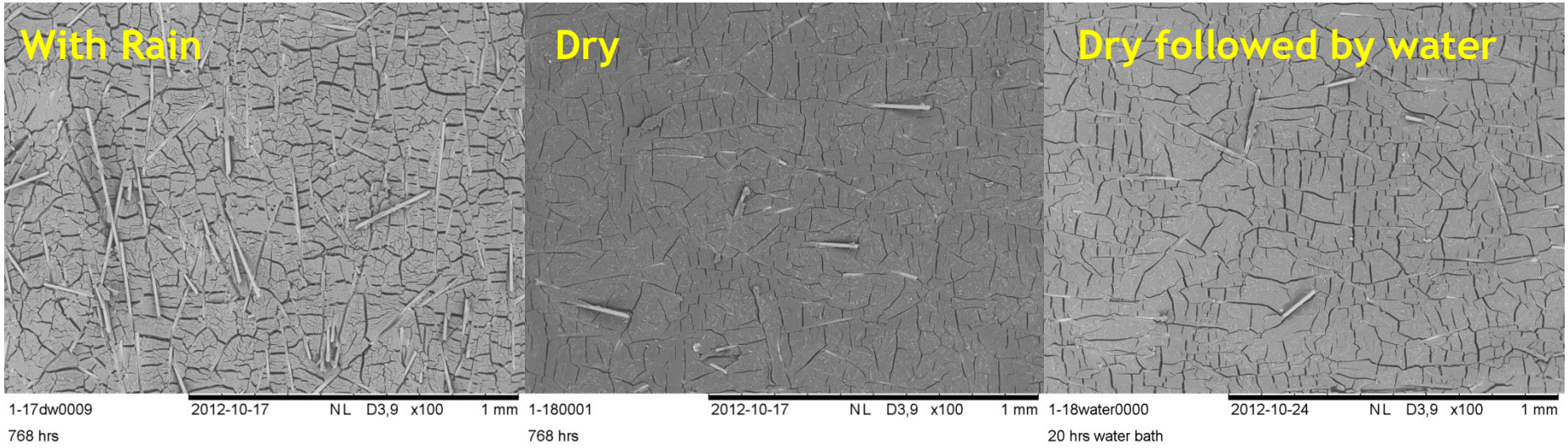


768 hrs



20 hrs water bath

Effect of water on crack formation during weathering of PA6 plaques



More glass fibers are visible after weathering with rain cycle.

Cracks are more pronounced after water treatment of dry sample, however, less glass fibers are exposed compared to a sample weathered with rain cycle.

This suggests that degraded material has been washed away.

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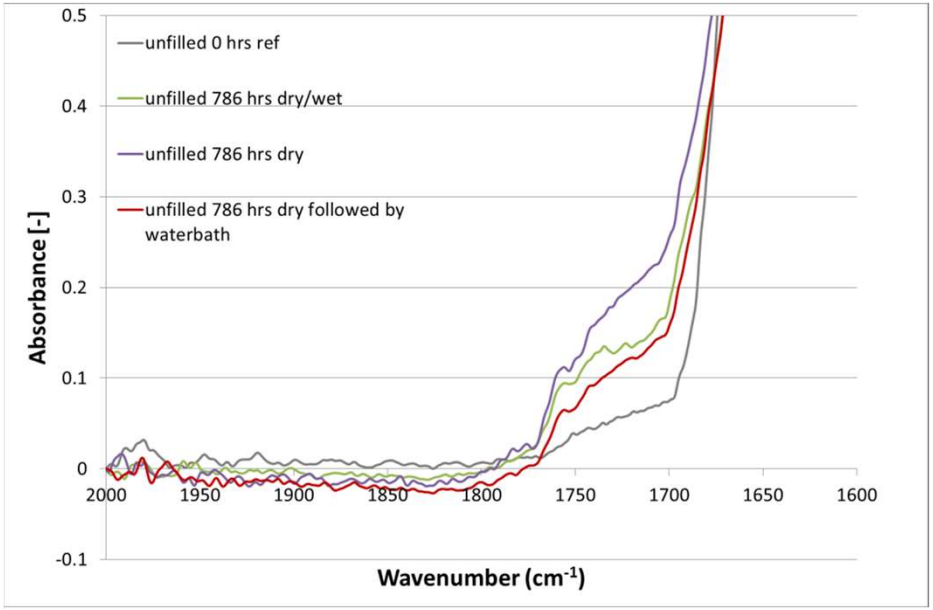
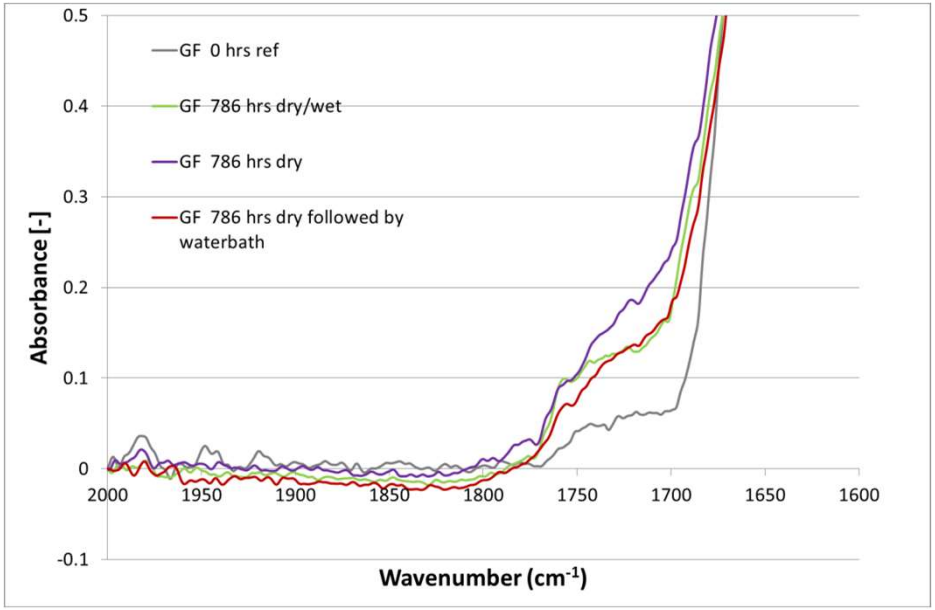
Influence water treatment on oxidation degree (Carbonyl absorption)





Water washes away oxidized polymer

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Influence moisture on weathering of Polyamides

- Conclusions:
  - Moisture and GF have no influence on the photo-oxidation rate of PA6
  - During ‘humid’ photo-degradation GFR PA6 form more cracks than unfilled PA6
  - Water treatment of dry aged plaques leads to more cracks more pronounced and higher amount)
  - Discoloration of GFR PA6 is a result of washing off degradation products (although an influence of water absorption/desorption on crack formation can not completely be excluded)

Conclusions

- Moisture plays an important role during weathering of polyamide 6

- Most plausible role of water:
  - washing away by photo-oxidation formed degradation

Acknowledgement

- Jacques Sampers
- Marjolein Diepens
- Manon Mak

for allowing me to present

You for listening

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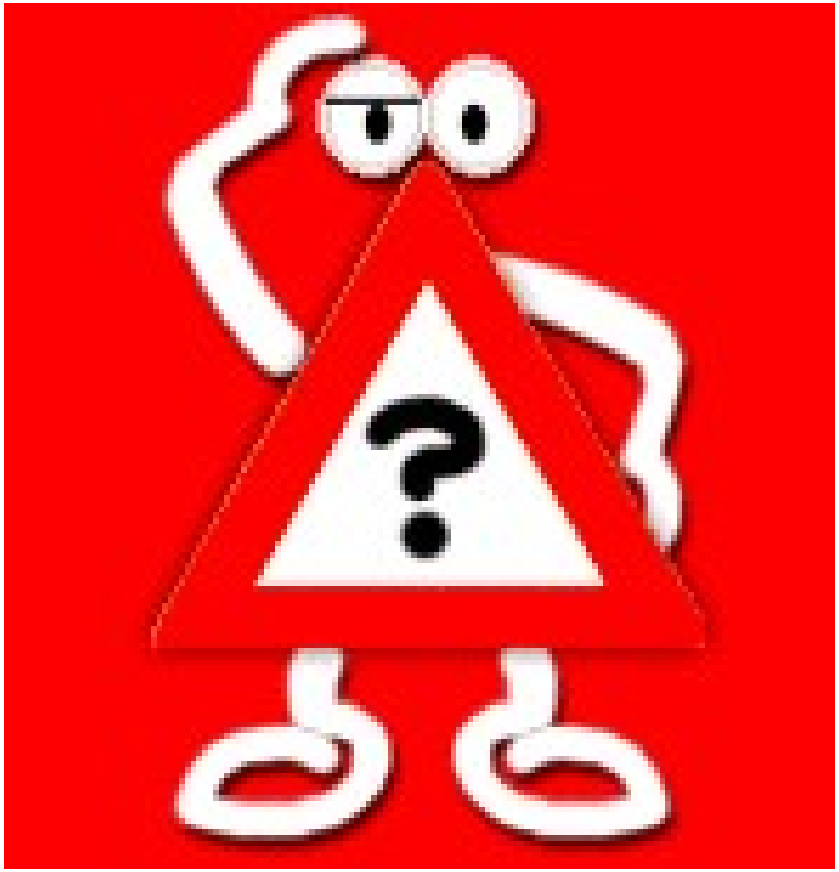
Questions



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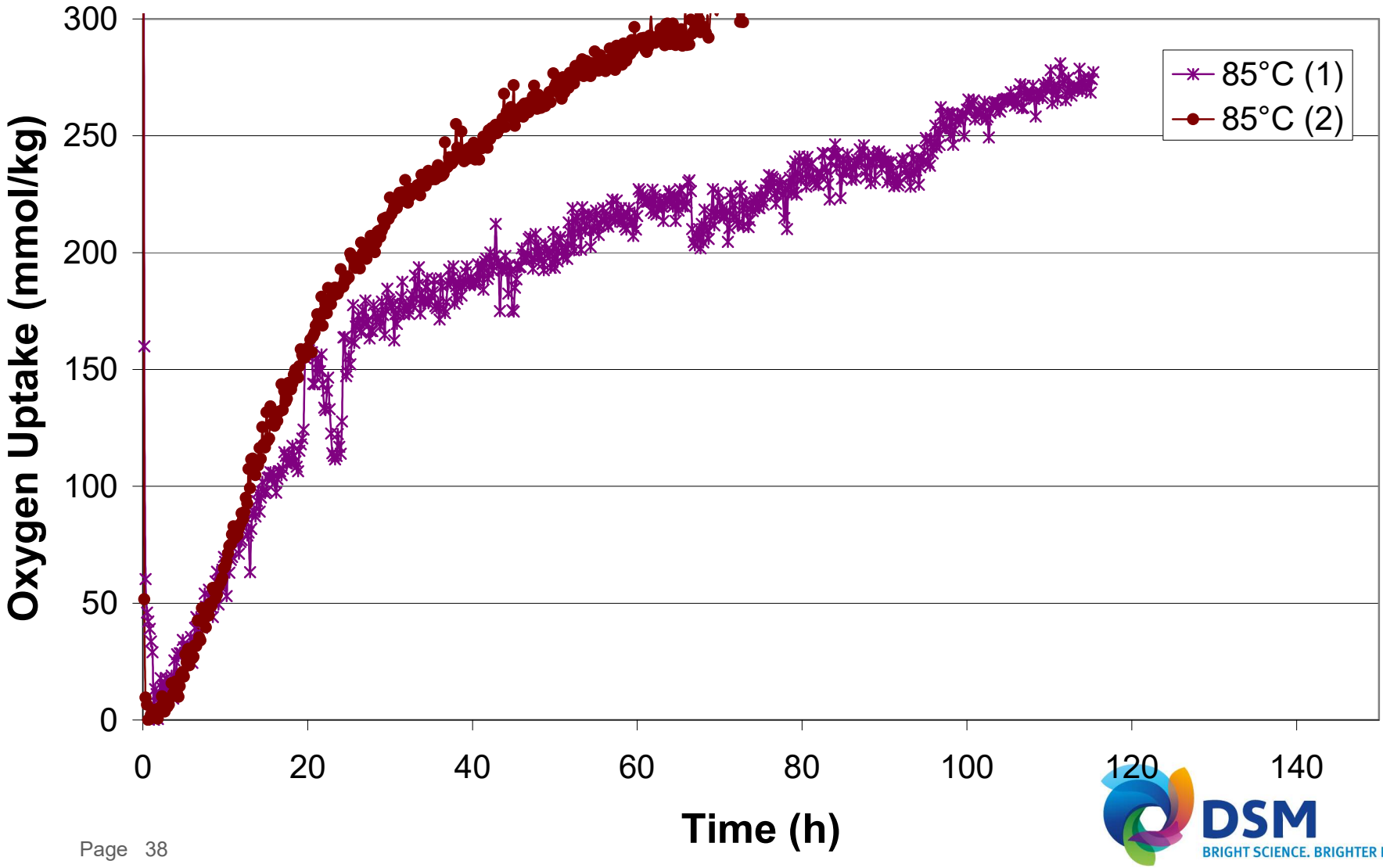
85°C/ 100% RH



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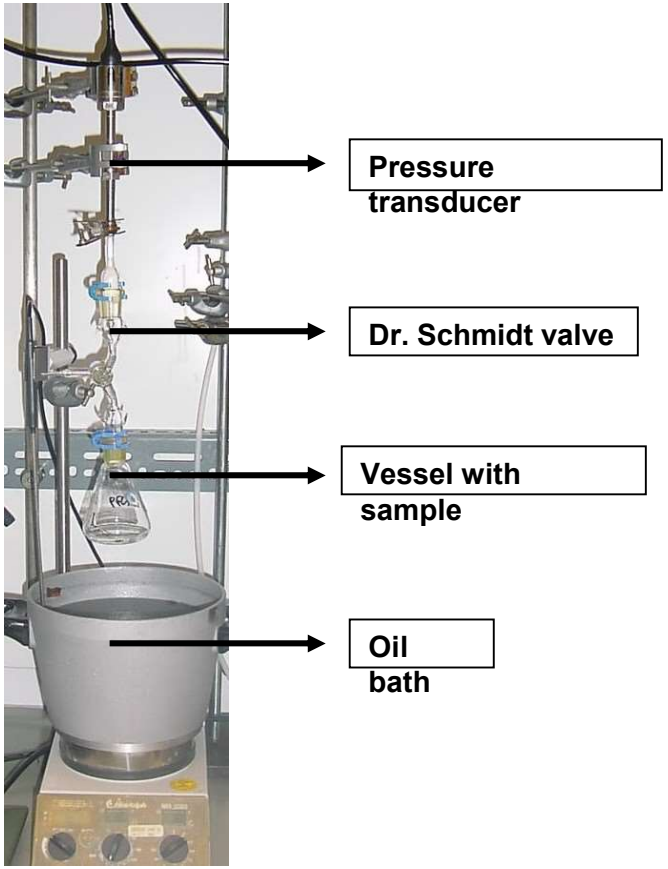
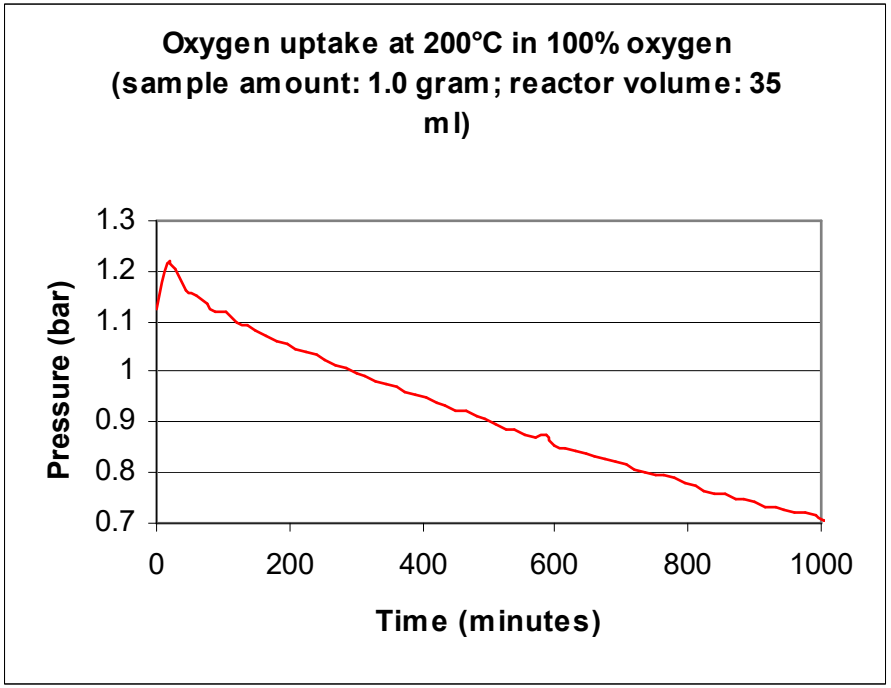
Oxygen uptake





The oxygen consumption is calculated from
the pressure drop

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2. Influence moisture on weathering of Polyamide 6

- Relation between outdoor weathering and accelerated weathering for a water absorbing (PA 6) and a non-water absorbing polymer (PP)
- Influence moisture and glass fiber reinforcement on the weathering of PA 6

J. Sampers, P. Gijsman, The influence of humidity/water on the weathering of polyamides, RD-00012930