ATLAS
MATERIAL TESTING SOLUTIONS

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MEASUREMENT & CALIBRATION TECHNOLOGIES

Weathering of Polypropylene New Technologies and Test Standards

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Introduction

- Flexible intermediate bulk containers (FIBCs) for non-dangerous goods

Introduction

- Paper from Allison Bouchat, BulkDistrubutor, FIBCs&Bagging March/April 2015
- "Testing the UV resistance of FIBCs"
- "Big bags are most commonly made of woven polypropylene, a polymer that, like other materials, is damaged by exposure to sunlight over time. This degradation process can ultimately cause the fabric to tear when exposed to strain and put both content and personnel at risk."
- "Fortunately, through the use of UV stabilisers in the polymer and the proper handling of FIBCs, the risk of photochemical damage can be reduced to a minimum."
- "It is, however, vital that FIBCs are covered or stored away from the sunlight during usage, transport and storage."

Introduction

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- Effect of photo oxidative ageing on (thermoplastics) polymers
- XX main criteria, X secondary criteria

criteria	PE, PP	PSMA	PM	PVC	POM	PA	PET	PC
yellowing	X	XX	XX	XX		X		XX
surface cracks chalking	X	X			XX			
tensile strength elongation at break	XX		X	X		XX	XX	
impact strength	X	X	XX	X	XX	X	X	X
bending strength		X			X		X	

Quelle: Krebs/Avondet/Leu: Langzeitverhalten von Thermoplasten Hanser-Verlag, München (1999)

Introduction

- ISO 21898: Packaging — Flexible intermediate bulk containers (FIBCs) for non-dangerous goods
- Annex A (normative) UV resistance test
  - *A.3 Apparatus*
    - The apparatus should be in accordance with ASTM G154-98, using a UV-B lamp.
  - *A.4 Procedure*
    - Expose a test specimen to a fluorescent UV lamp for at least 200 h, using a test cycle of 8 h at 60 °C with UV radiation, alternating with 4 h at 50 °C with condensation.
    - After exposure is complete, test the specimen for breaking force and elongation at break in accordance with ISO 13934-1 using the conditioning requirements given in 5.2.2. Compare the values with results performed on simultaneously cut test specimens that have been stored under dark and cool conditions.
  - *…………*

Introduction

- What are the environmental stress factors for FIBCs?
- Made of woven PP
- Colors white and red

Weathering

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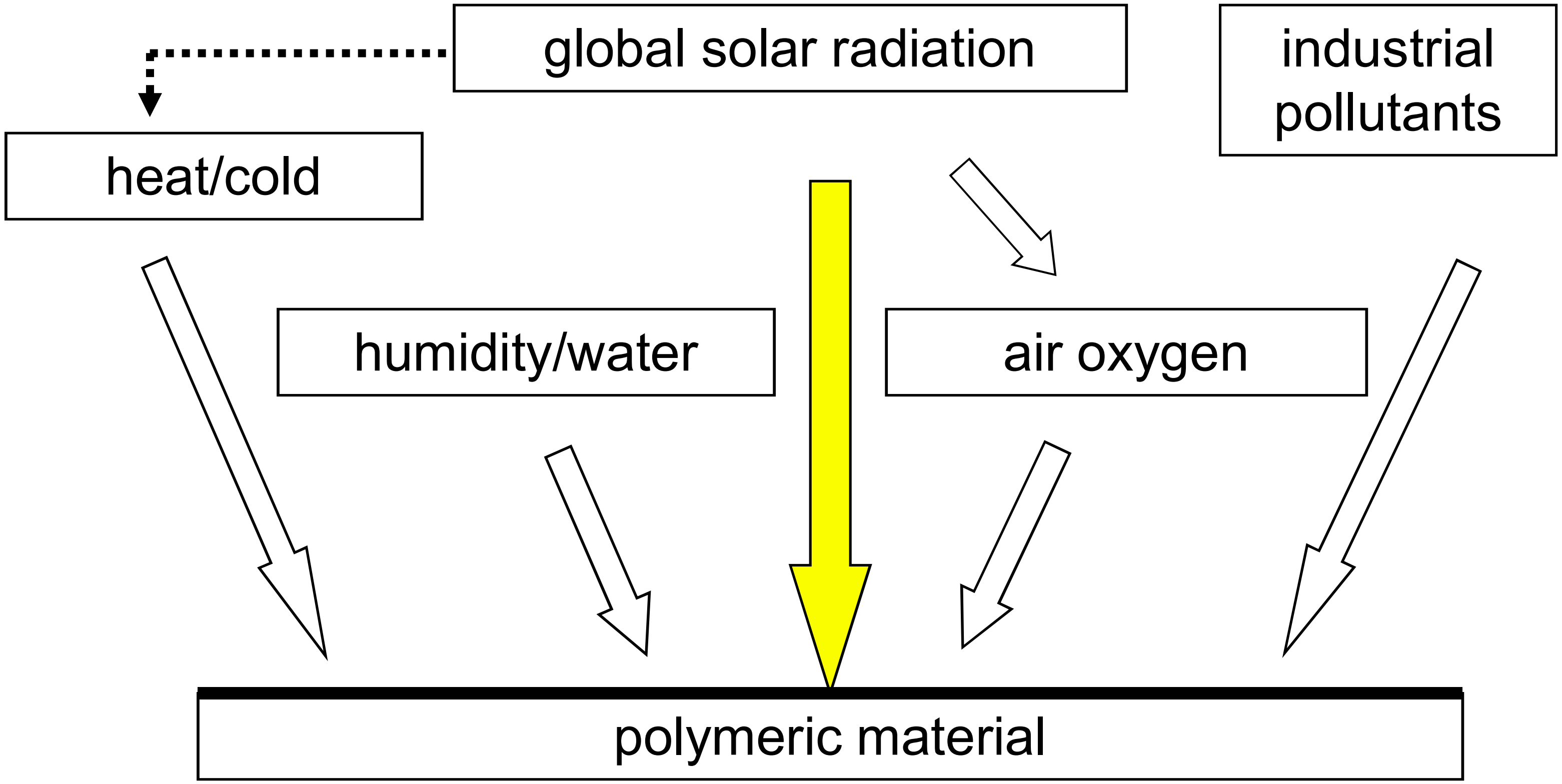


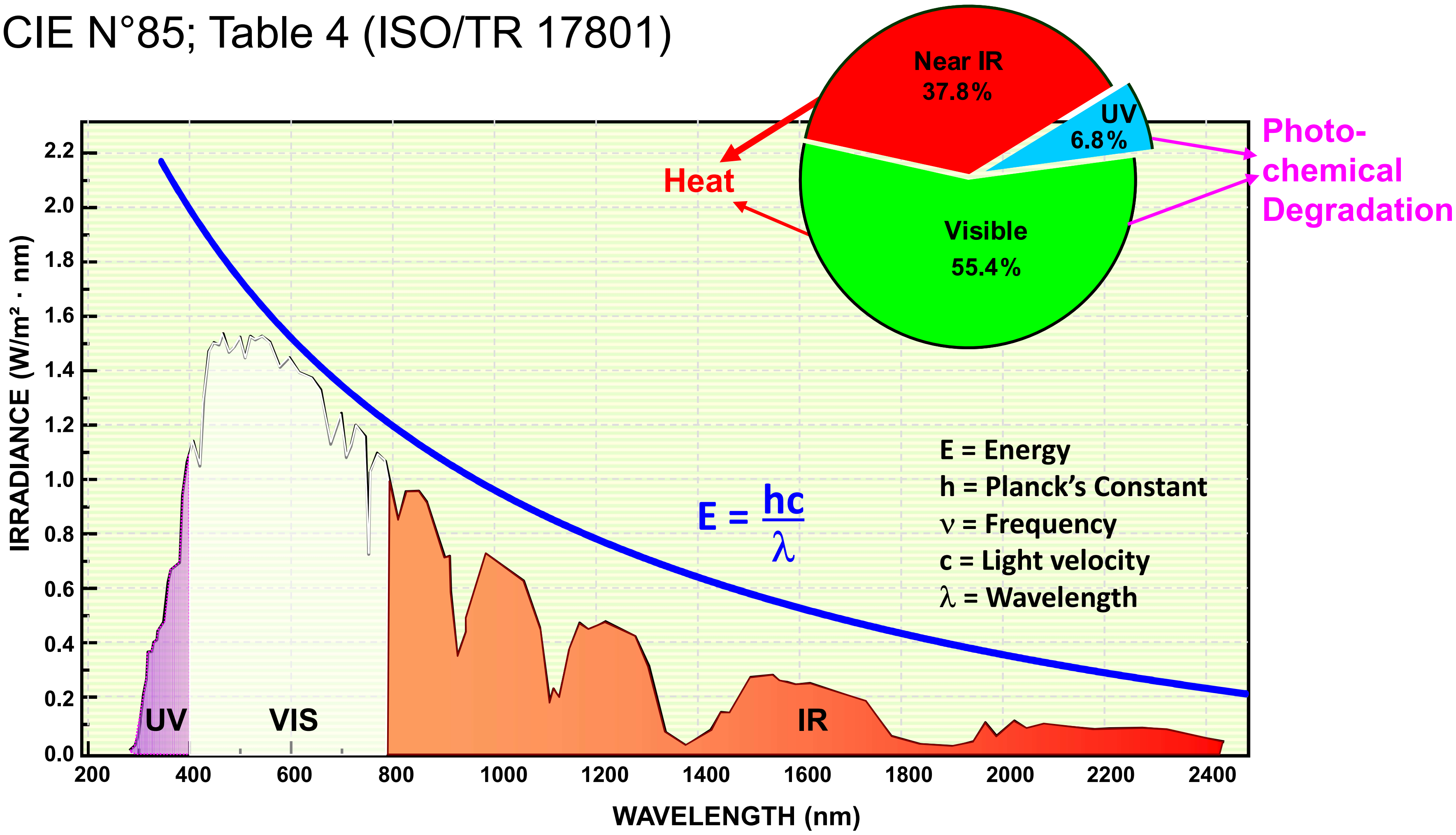
Factors of weathering

- Spectral irradiance distribution
  - $f_{SPEKTRUM} = E_{e\lambda}(\lambda)$
- Irradiance (W/m²)
  - $E_{UV} = E_e = \int_{300\ nm}^{400\ nm} E_{e\lambda} \cdot d\lambda$
- Sample temperature
- Black standard temperature (°C)
  - *Measure for maximum temperature of samples*
- Ambient air temperature (°C)
  - *Measure for minimum temperature of samples*
- Relative Humidity (%)
- Water (rain, dew)




Radiation effect: solar radiation

- Spectral irradiance distribution of global solar radiation (AM 1):
- CIE N°85; Table 4 (ISO/TR 17801)

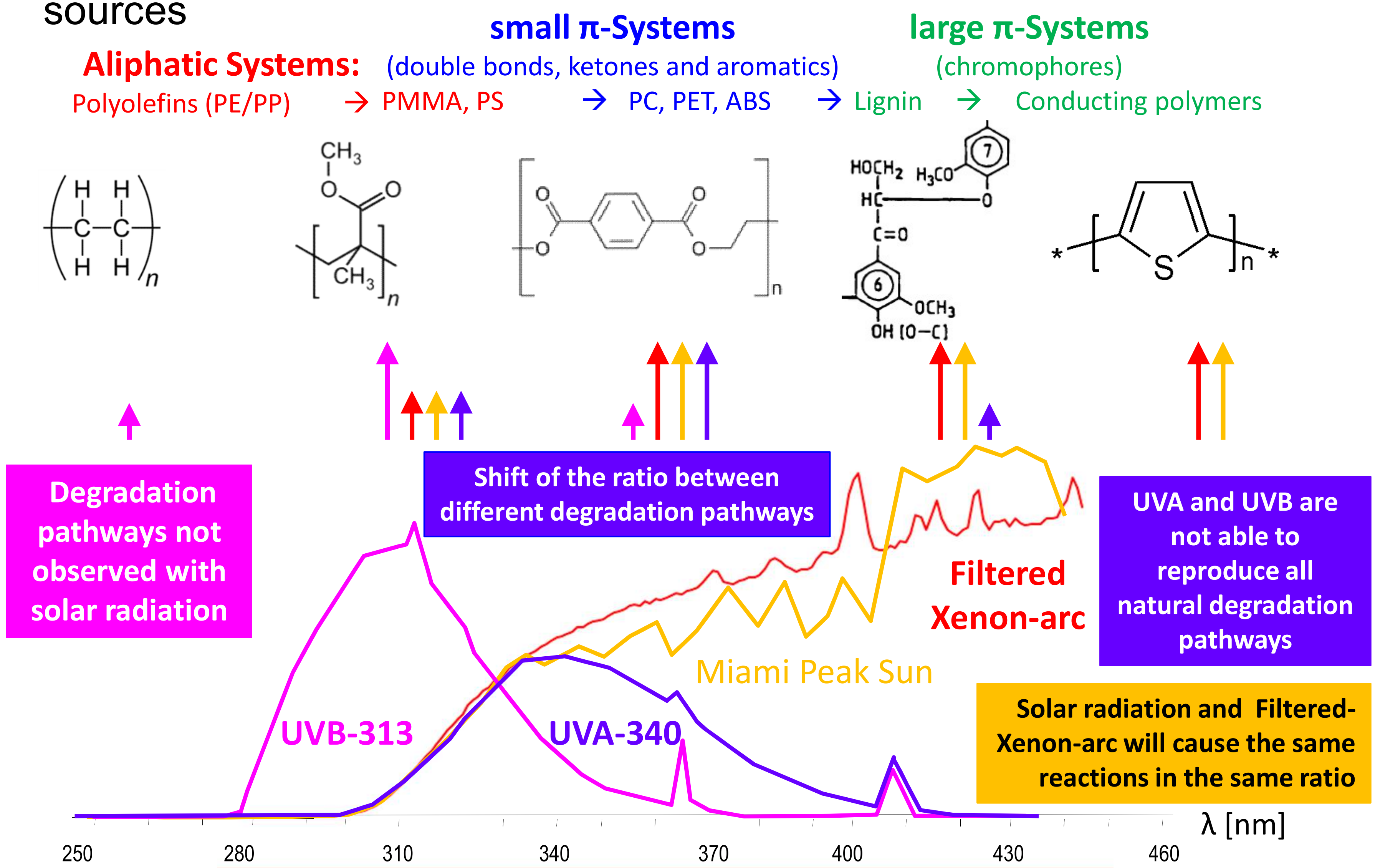


Radiation initiated ageing processes

- Photolysis
  - *ageing processes, without participation of O_2*
  - *example PVC: HCl separation, leads to yellowing and later to browning*
- Photo-oxidation
  - *ageing processes, with participation of O_2*
  - *example polyolefin: emerging ketenes, carbon acids, vinyl groups, chain scissions, CO_2, H_2O*
  - *example polypropylene: oxidation can continue after a radical chain reaction – auto-oxidation*
- Photo-catalysis
  - *example: radiation absorption by pigments with semiconductor properties*

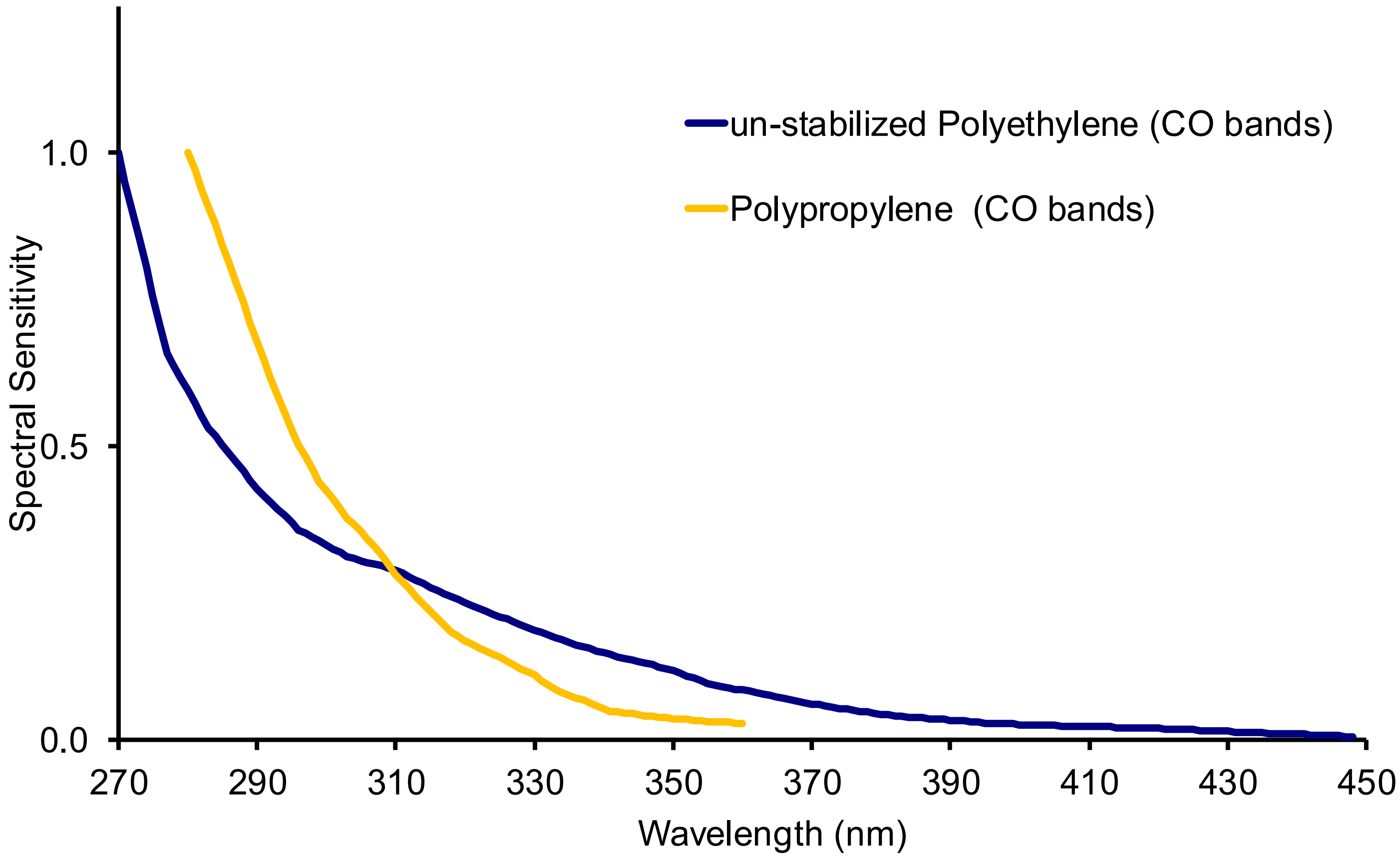
Radiation effect: spectral sensitivity

- Spectral sensitivity of pure polymers matrixes compared with radiation sources



Radiation effect: spectral sensitivity

- Action spectra (spectral sensitivity) of an un-stabilized polyethylene foil and a 270µm thick un-stabilized polypropylene foil



A. Geburtig et al. BAM, Berlin, VFI

Radiation effect: spectral sensitivities

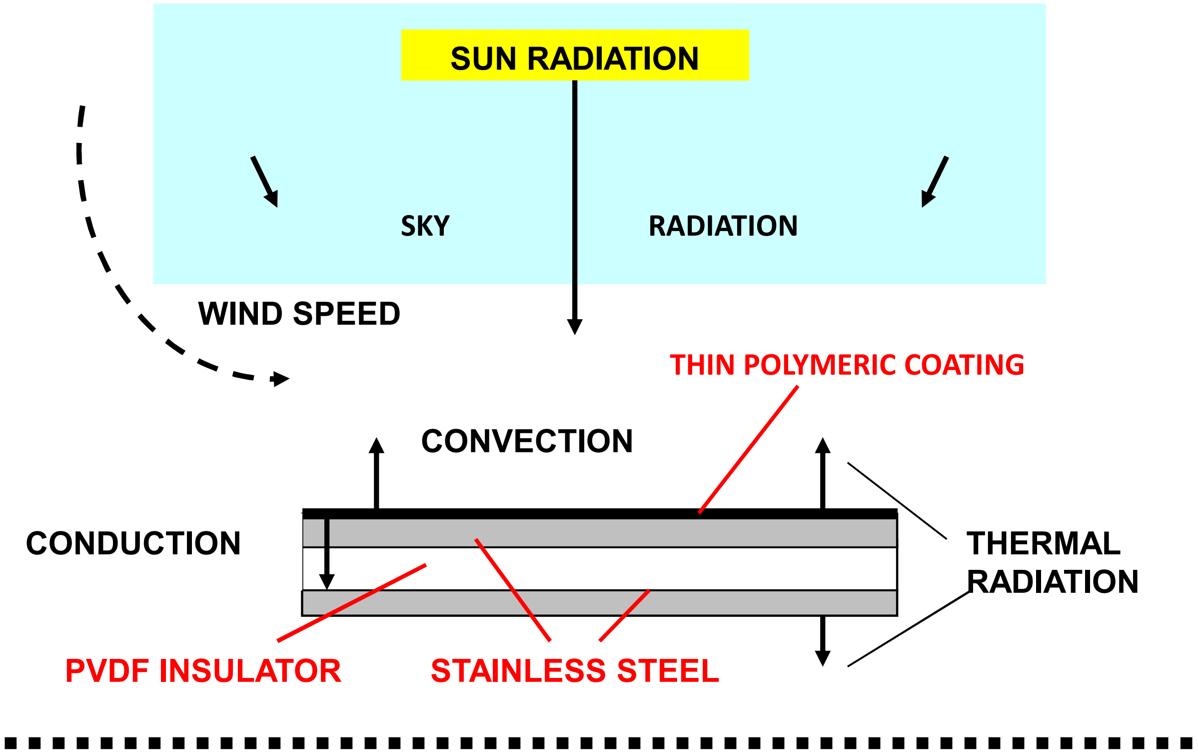
- Examples of spectral sensitivities (Norma D. Searle, SunSpots Volume 24 Issue 48, 1994)

ACTIVATION SPECTRA*			
Polymer	Mils	Solar region causing maximum degradation	Type of degradation
ABS	100 10	350-380nm >380nm >380nm 370-385nm	loss in tensile strength loss in tensile strength (longer exp.) bleaching (decrease in yellowness) increase in UV absorption (long exp.)
Polyacrylate	60	385nm	increase in yellowness
Polyamides (aromatic)	film/fibre	360-370nm*, 415nm*	increase in yellowness
Polypropylene	15 60	340-380nm 360-380nm	carbonyl formation loss in tensile strength (long exp.)
Polyurethanes (aromatic)	film	350-415nm*	increase in yellowness
PVC copolymer with vinyl acetate	film	365nm	increase in yellowness and increase in UV absorption
*Range of activation spectrum varies with formulation			

*Norma D. Searle, Handbook of Polymer Degradation

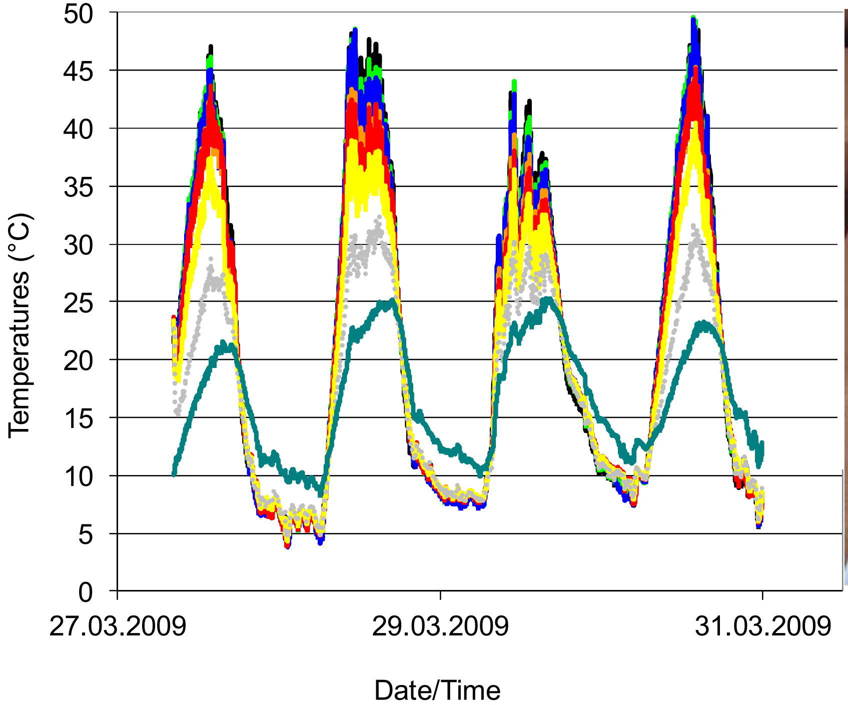
Temperature effect by irradiation

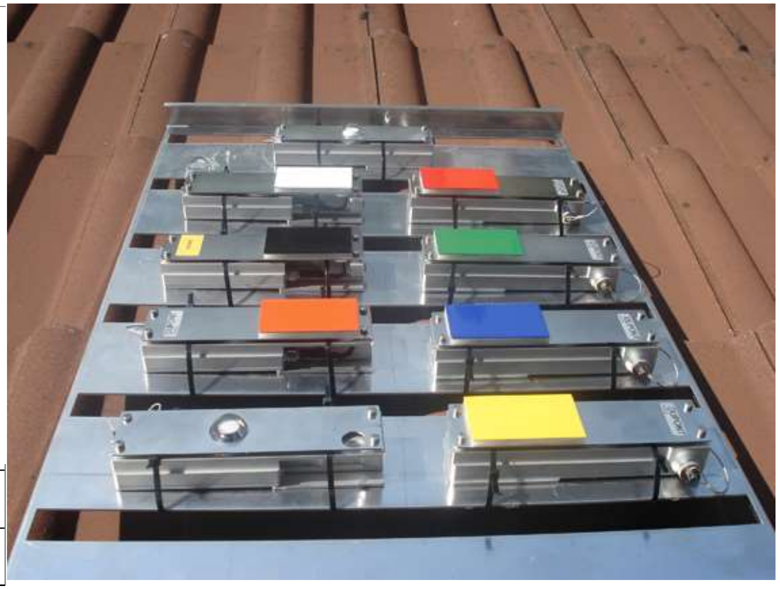
- Schematic drawing of a coated isolated stainless steel plate which is exposed to the natural weather factors sun radiation, ambient air temperature, and wind



Temperature effect by irradiation

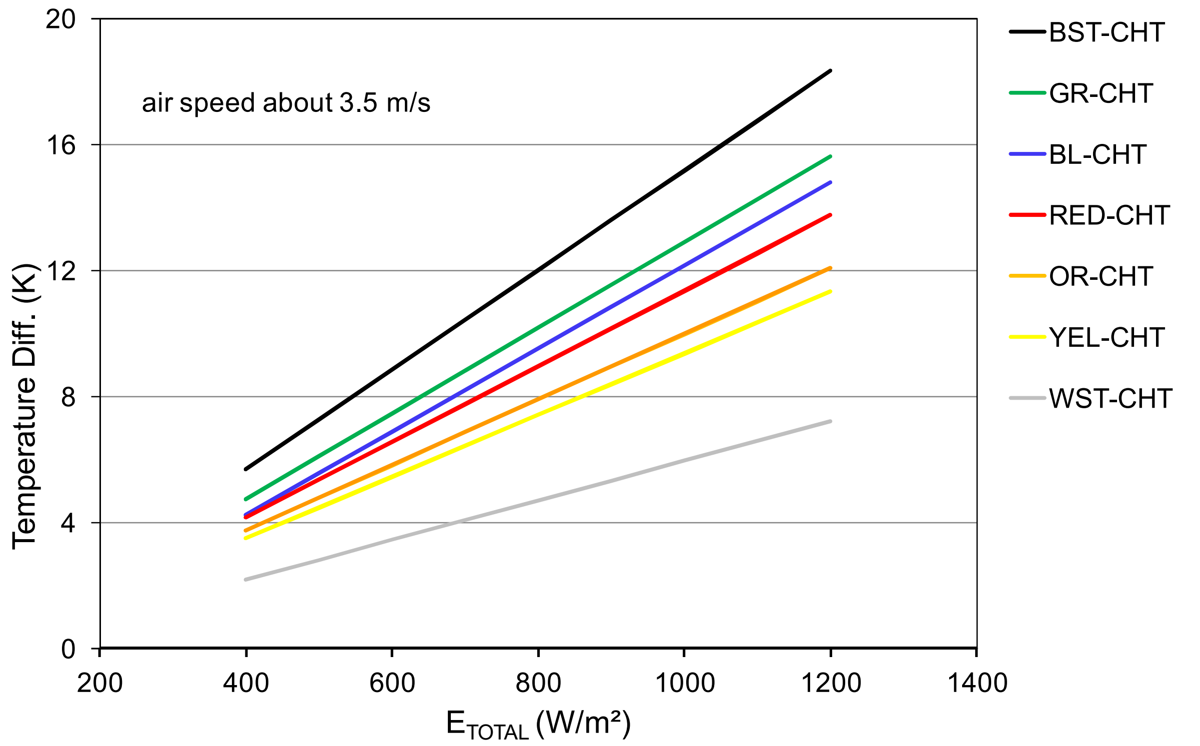
- Surface temperatures and ambient air temperature in central Arizona mostly clear days (data every minute)
- colored surface temperature sensors at on orientation of 45° to the horizontal





Temperature effect by irradiation

- $\Delta T = T_{SURFACE} - T_{AMBIENT}$ = COLOR-AMB (Set A)
- v_{WIND} ca. 3.5 m/s
- Xenotest Beta (global solar radiation filter acc. CIE85, Tab.4)



Temperature effect by irradiation

- **Xenon**
- technology reproduce the same temperature effect as solar radiation
  - *amount and temperature separation*

- **Fluorescent UV**
- will not effect specimen temperature in the way as solar radiation
  - *no temperature separation*
  - *a temperature increase by thermal radiation is possible*

Temperature effect on photochemical reaction

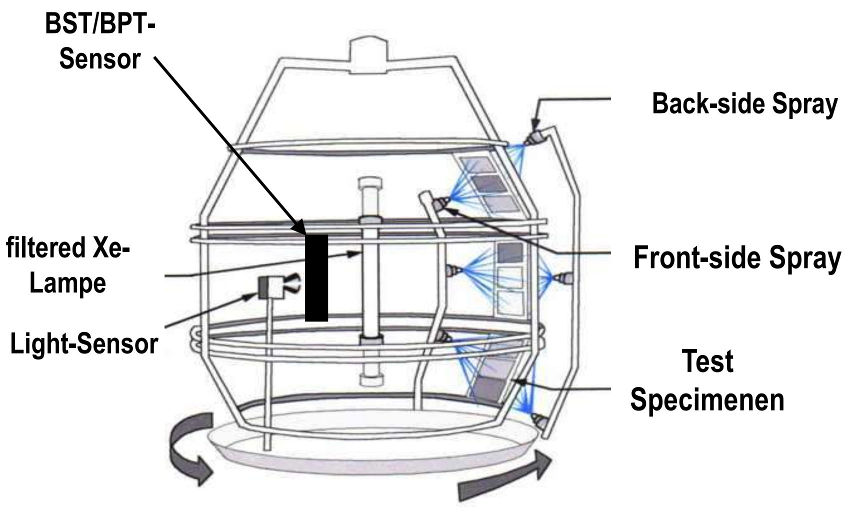
- Effects that depend on temperature
  - *moisture and oxygen diffusion*
  - *stabilizer diffusion*
  - *reaction rate of photochemical reaction*
  - *reaction rate of secondary reactions*
  - *material properties (e.g. glass transition, melting point …)*
  - *mechanical effect of temperature and temperature cycles…*
- If similar samples are tested and temperature separating can be neglected external temperature control in **Fluorescent UV** instruments might be sufficient
- Differences in the degradation behavior of differently colored species, as observed in nature, can only be reproduced with **Xenon-arc** radiation

Water – effect (mechanical, chemical)

- Water as
  - *Humidity; rain; dew*
- Effects
  - *Change of T_G (mobility of O_2 and H_2O)*
  - *Extraction of additives (UV-Absorber, Antioxidants)*
  - *Mechanical stress by*
    - Abrasion, blistering by impinge
    - Swelling - shrinking
  - *chemical reaction of the material with water*
    - Hydrolysis (PA, PU)
    - Generation of OH und HO_2 – radicals by irradiation, which react with the organic material

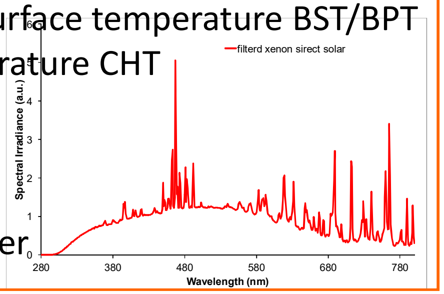
Technical principles: instruments

Xenon-arc (Rotating Rack)

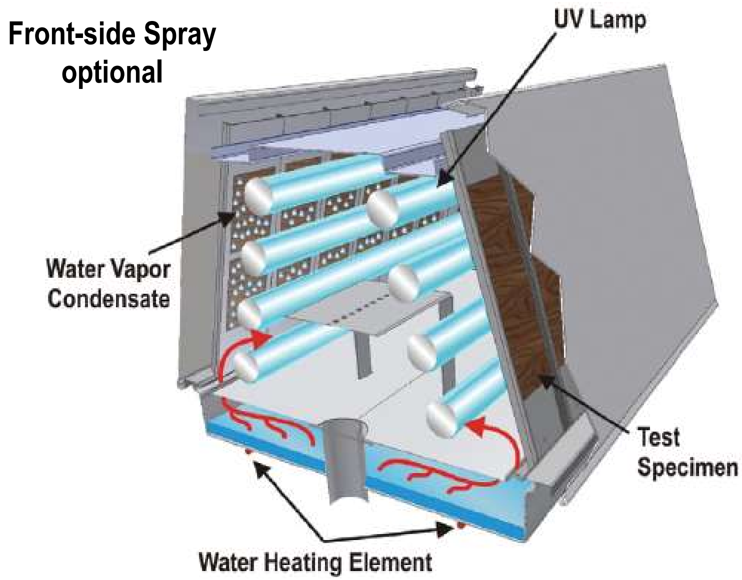


Environmental control

- SID by optical filters
- Irradiance control
- Temperature control:
  - Reference sensor surface temperature BST/BPT
  - Chamber air temperature CHT
- Humidity Control
- Water sprays
- Light/Dark Cycling
- cooling by air-flow or chiller

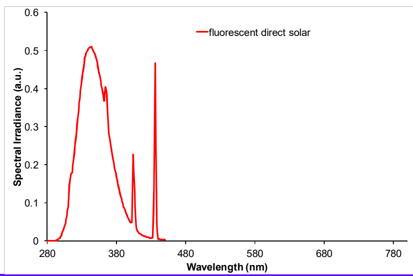


Fluorescent UV



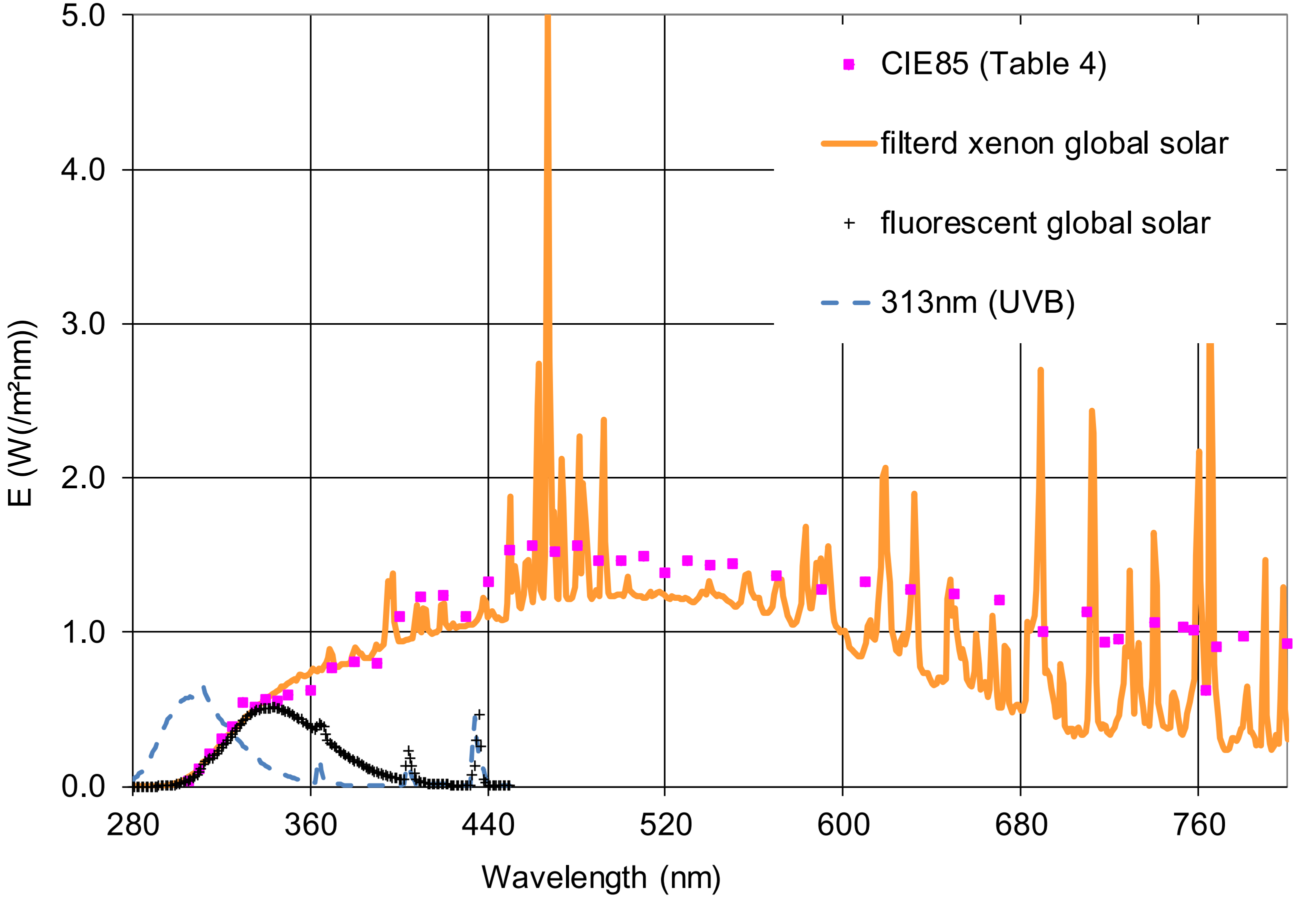
Environmental control

- SID by lamp type
- Irradiance control
- BPT control
- external heater
- Water sprays
- Condensation (dark cycle)
- Light/Dark Cycling



Simulation of global solar radiation

- Fluorescent 313 nm (UVB) is not a simulation of global solar radiation



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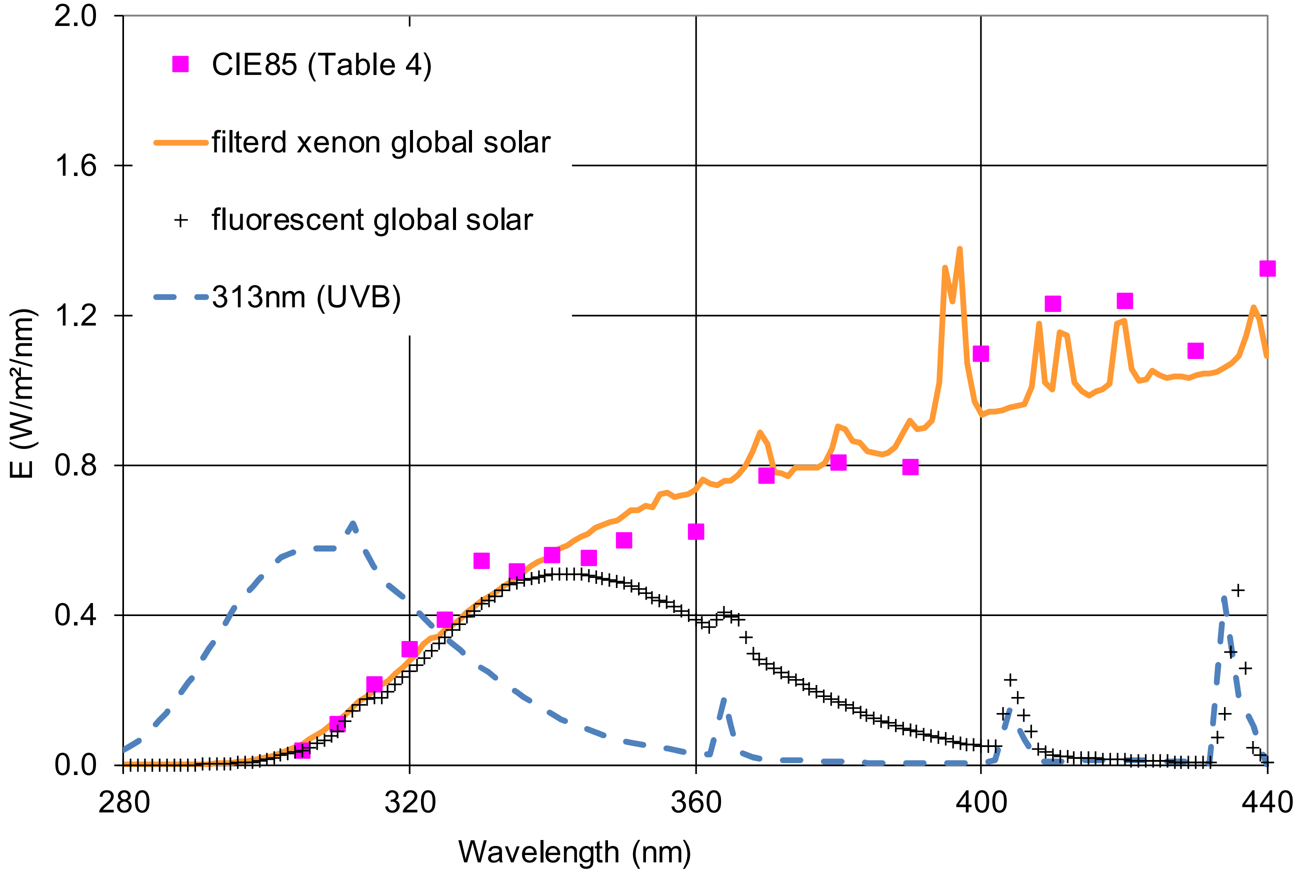
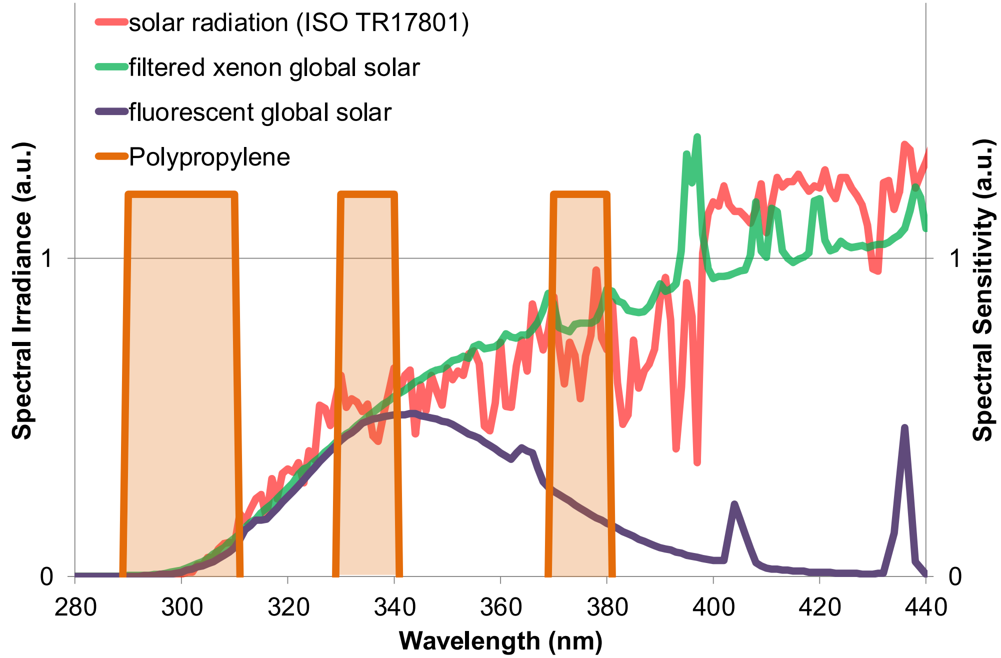


Activation spectra of polypropylene

- Descriptive presentation of ranges of spectral sensitivities of polypropylene
  - *yellowness (about 310 nm)*
  - *CO formation (about 340 nm)*
  - *Loss in tensile strength (about 380nm)*

- Global solar radiation
- Filtered xenon radiation
- Fluorescent radiation



Norma Searl Handbook of Polymers

Moisture effects: some comments

- The effect of moisture (water) can be simulated in both instrument technologies
  - *Since the two instrument technologies have spray function or allow condensation*

- Some instrument manufacturer argue that condensing humidity is more aggressive and more realistic then water spray
  - *Surface temperature effect can be different during condensation and spray*
  - *To the surface migrated reaction products are not removed by condensation*
- But there is no relevant publication available which confirm both effects

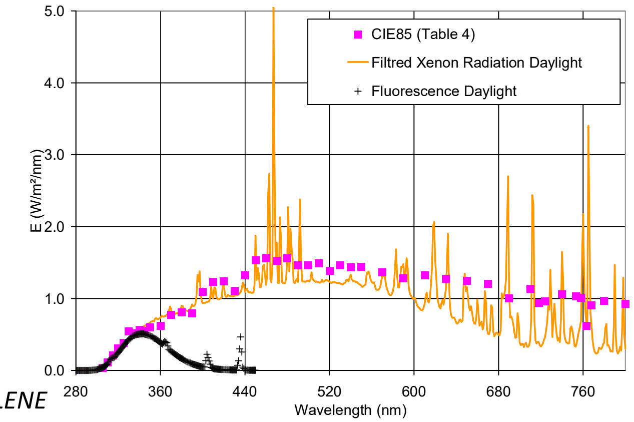
- Control of humidity can be important (only xenon technology)
- Instruments with fluorescent UV arc lamps do not control humidity

Example: PP with different stabilizer contents

- Geo textiles PP with different stabilizer contents:
  - *Laboratory weathering test in accordance to EN 12224 (Geotextiles and geotextiles-related products - Determination of the resistance to weathering), fluorescent method*
  - *Fluorescent UV device UV-A 340 arc lamp:*
    - UV2000 - irradiance E_{UV}: 38 bis 42 W/m² (0,83 W/m2 @ 340 nm), BPT: 50°C

      cycle: 5 h, 1 h spray @ ca. 30 °C (no UV)
  - *Xenon device*
    - Suntest XXL+ - irradiance E_{UV}: 40 ± 2 W/m², CHT: 20 °C, RH: 20 %, BST: 50 °C

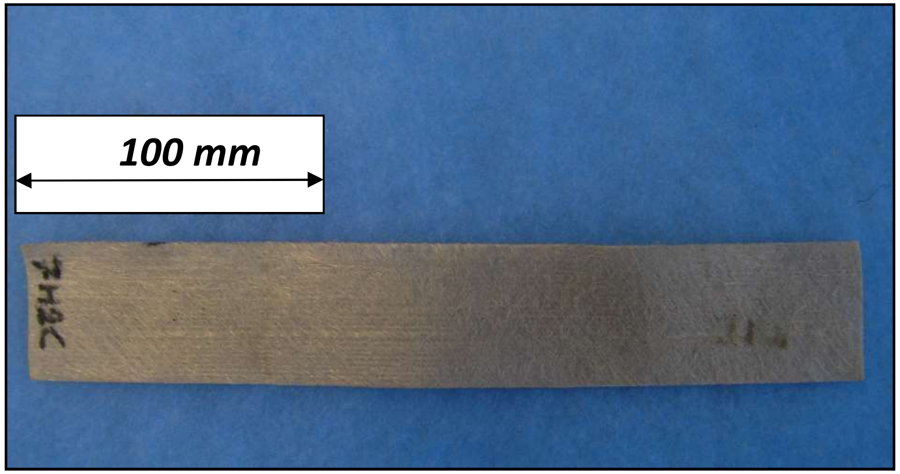
      cycle: 5 h irradiation, 1 h spray
  - *Natural weathering*
    - Würzburg (Germany),
    - Sanary-sur-Mer (France),
    - Hoek van Holland (The Netherlands)

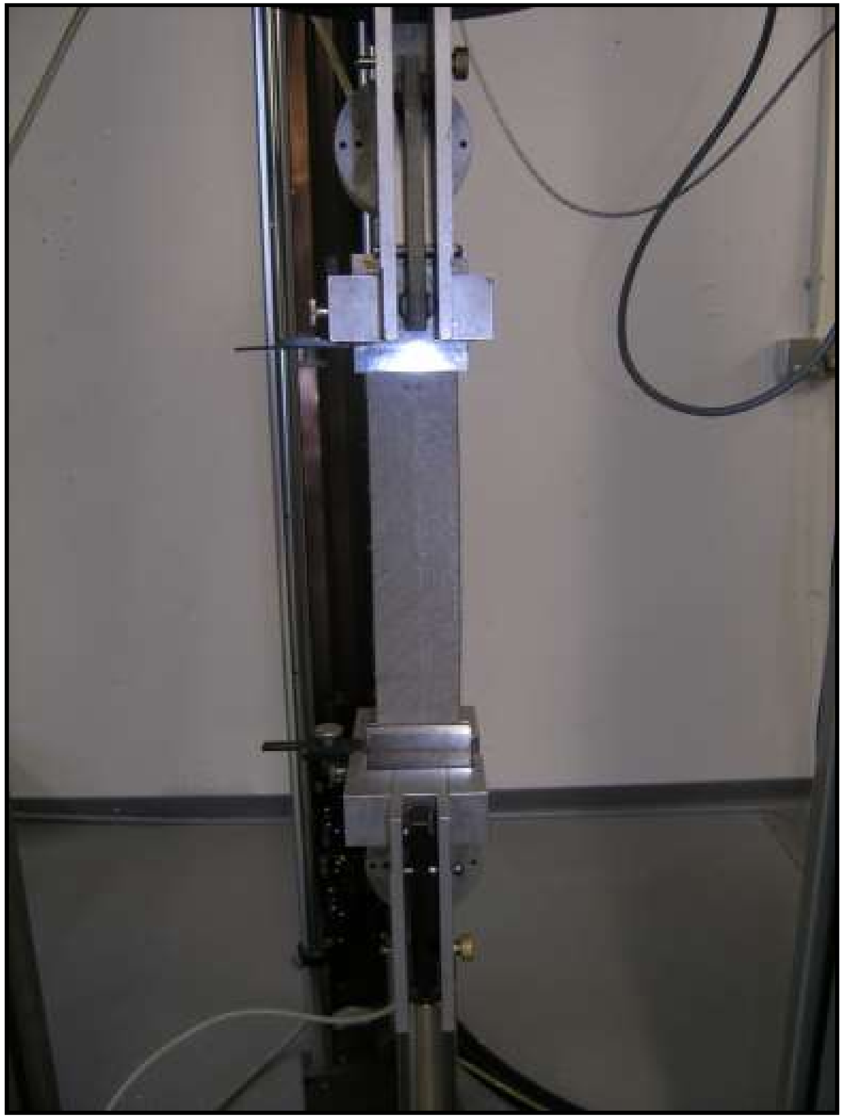


Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES“,EuroGeo4, 2008

Example: PP with different stabilizer contents

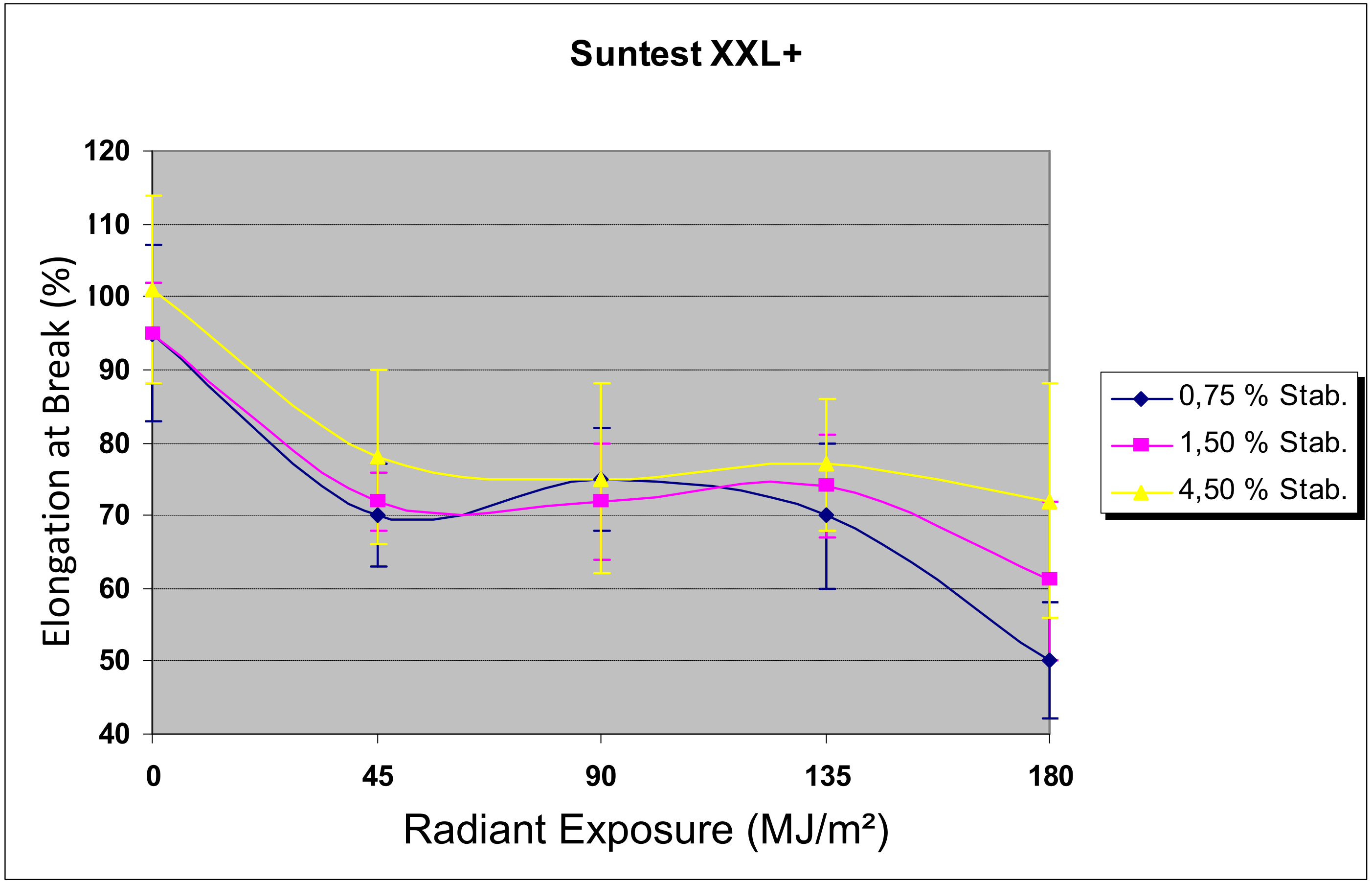
- Geo-textiles PP with different HALS stabilizer contents: 0.75%, 1.5%, 4.5%
- Mould proving 45 MJ/m² (total UV)
- Evaluation: tensile strength, remaining stabilizer content





Example: PP with different stabilizer contents

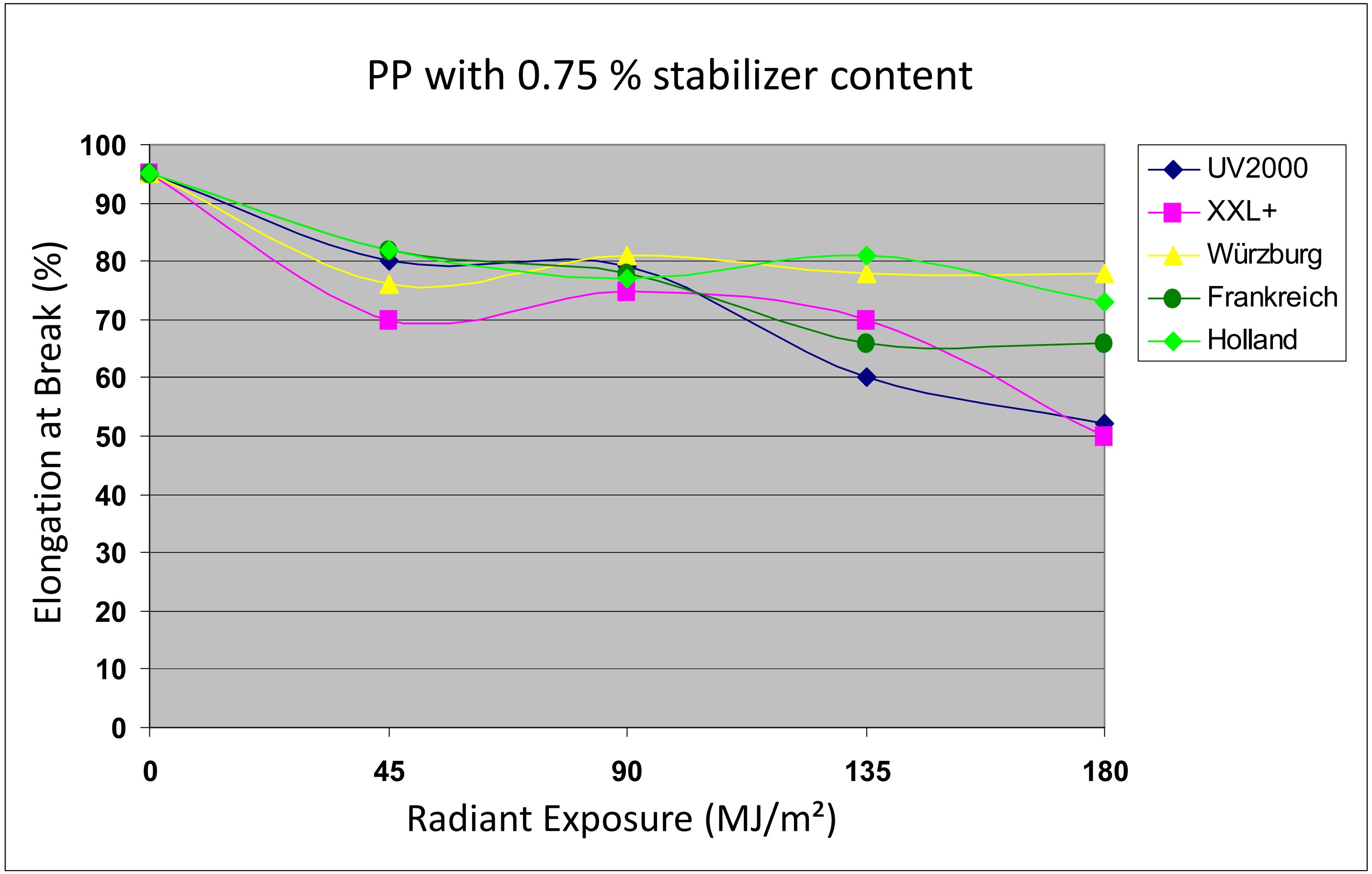
- Elongation at break after exposure in a Suntest XXL+



Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES“,EuroGeo4, 2008

Example: PP with different stabilizer contents

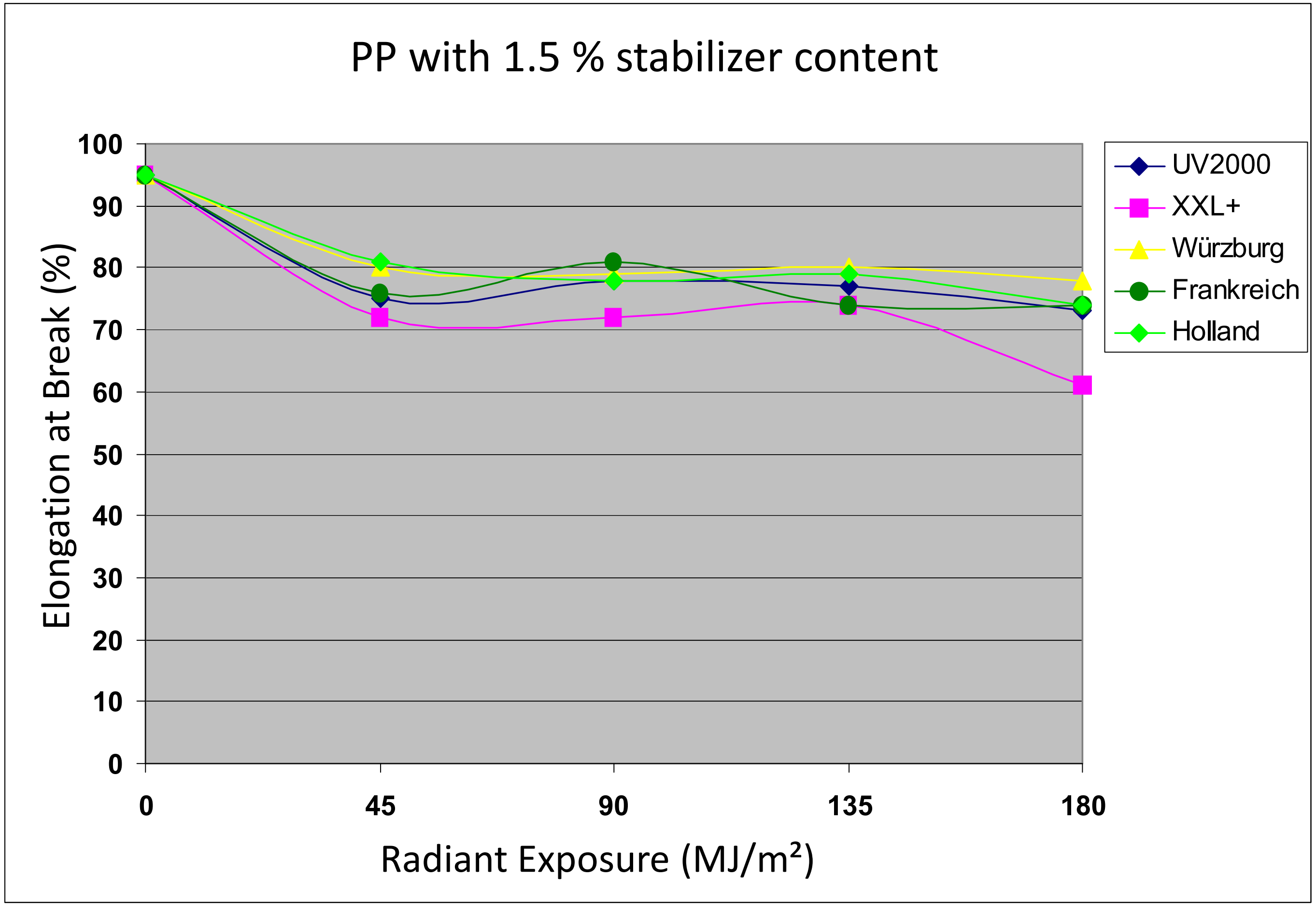
- Different locations and instruments at 0.75 % stabilizer content



Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES",EuroGeo4, 2008

Example: PP with different stabilizer contents

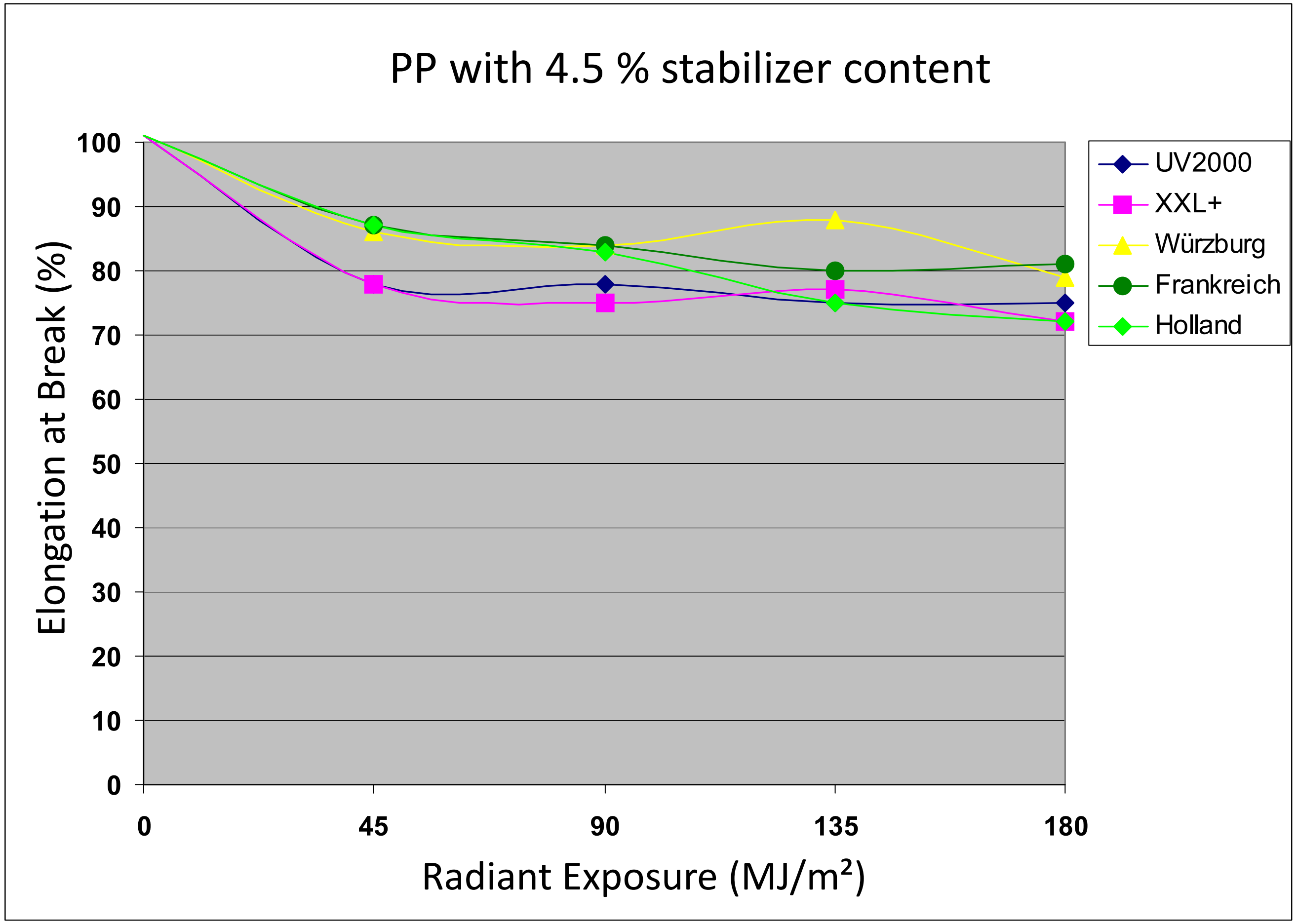
- Different locations and instruments with 1.5 % stabilizer contents



Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES“,EuroGeo4, 2008

Example: PP with different stabilizer contents

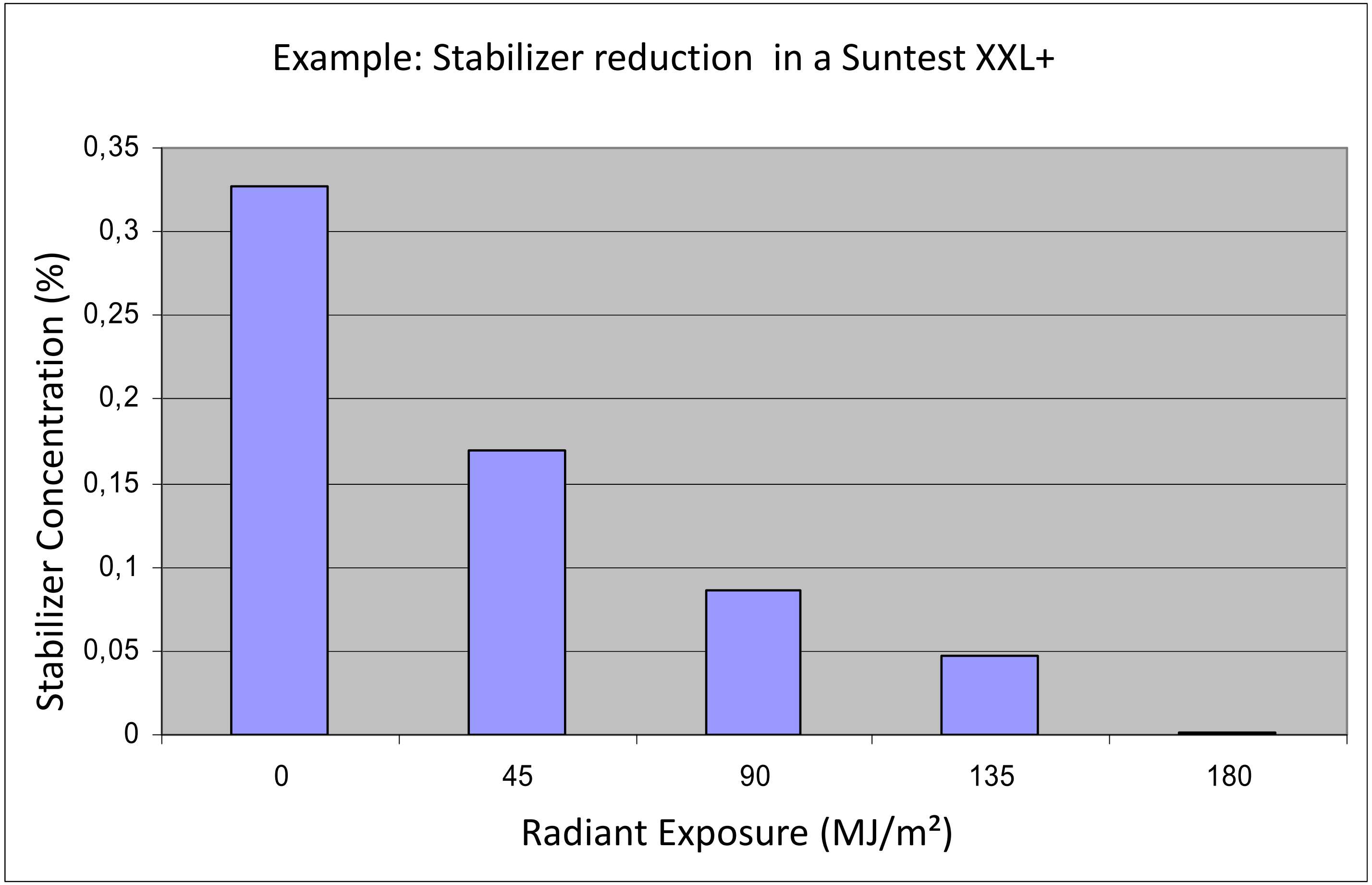
- different locations and instruments at 4.5 % stabilizer content



Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES“,EuroGeo4, 2008

Example: PP with different stabilizer contents

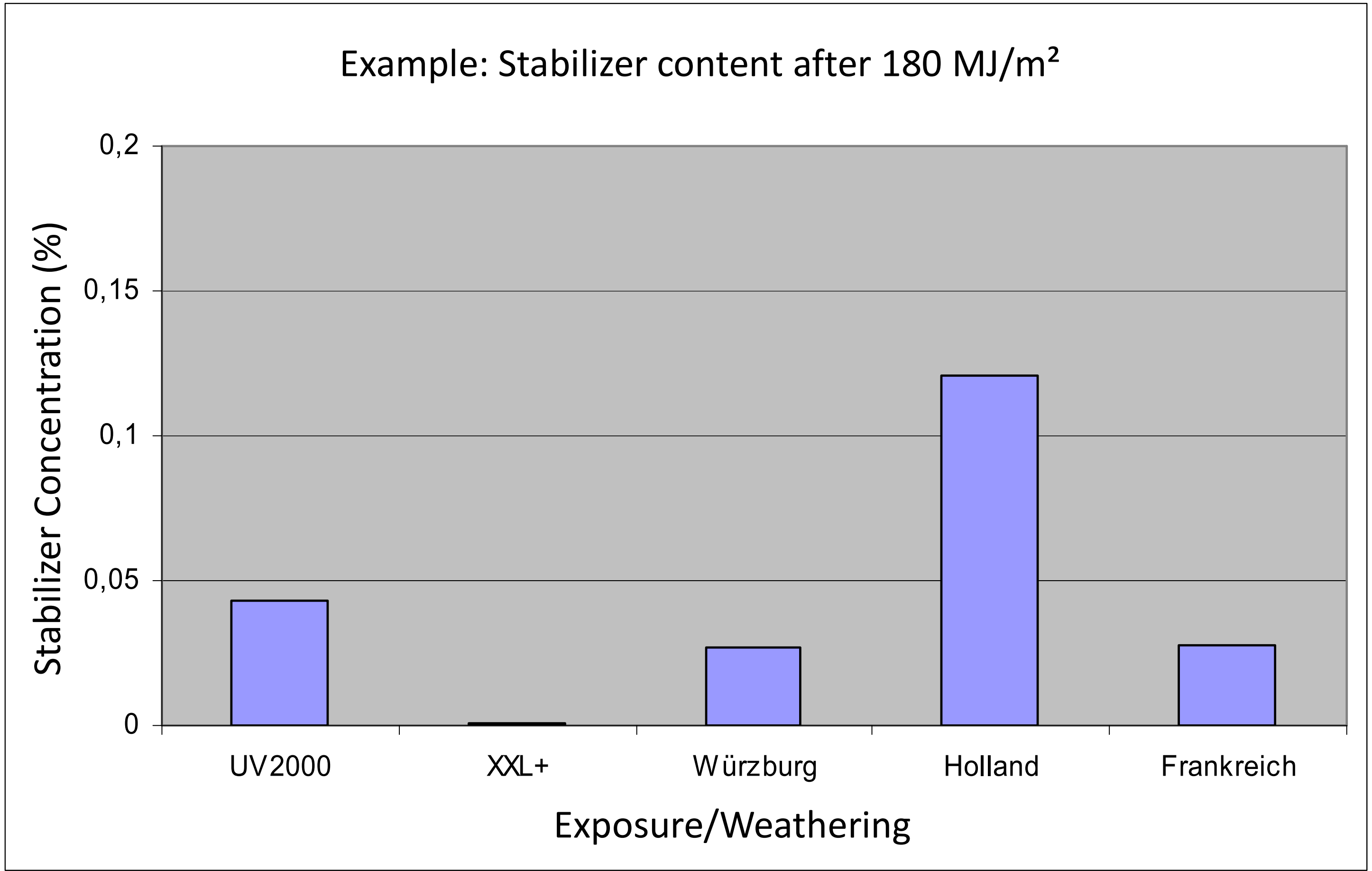
- Stabilizer consumption is a function of radiant exposure



Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES",EuroGeo4, 2008

Example: PP with different stabilizer contents

- Stabilizer content after 180 MJ/m² exposure



Marcus Heindl et all, „STUDY OF ARTIFICIAL AND OUTDOOR WEATHERING OF STABILISED POLYPROPYLENE GEOTEXTILES",EuroGeo4, 2008

Summary

- A weathering test for FIBCs is described in ISO 21898 with a fluorescent UVB radiation source.
  - *The UVB radiation source seems not to be an ideal solution because of the wavelength below 290 nm which does not exist in global solar radiation.*
- Regarding the spectral sensitivity of PP the use of a fluorescent
  - *UVA radiation source can be appropriate*
  - *better a xenon laboratory radiation source*
- The temperature separation observed during natural exposure can be reproduced in a
  - *xenon weathering device*
  - *but not in a fluorescent UV device*
- Modern instrument shall generate, measure and, control UV irradiance, the temperature level and, relative humidity.