How do polymers degrade in Antarctica?

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&

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Environmental testing - Weathering

Polymer weathering:

Effect of environmental impacts on polymer properties
Verification of ability to withstand intended application
Almost realized in localities with high intensity of solar radiation

- **Solar radiation**
- **Temperature**
- **Humidity**
- **Rain**
- **Mechanical stress**
- **Air-pollutions**

All varying
in intensity and time

Pilot localities used for polymer testing (yearly doses):

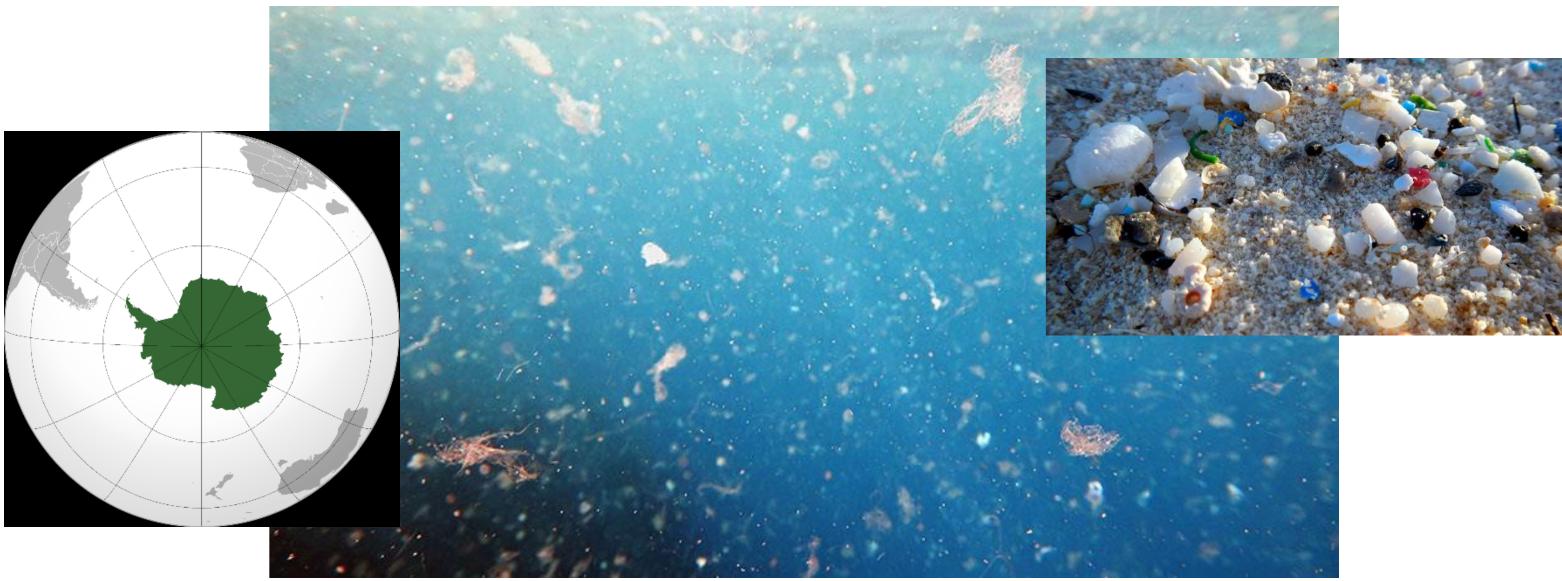
Florida	**140 kLy**	**(marine, wet)**
Arizona	**180 kLy**	**(continental, dry)**
Bandol, F (south EU)	**120 kLy**	**(marine, wet)**
Basel, Swiss (middle EU)	**90 kLy**	**(subcontinental, mild)**

Weathering tests provide the most reliable information on polymer durability under the real climatic conditions of application.

In general, weathering of polymers may be carried out anywhere on the planet !

Why Antarctica?

- **High social attention to marine pollutions caused by plastics in general**
- **Commodity polymers particles found as microplastics by the coast of Antarctica**



Questions: **What happens with polymer exposed to Antarctic climate ?**

How long will it remain there ?

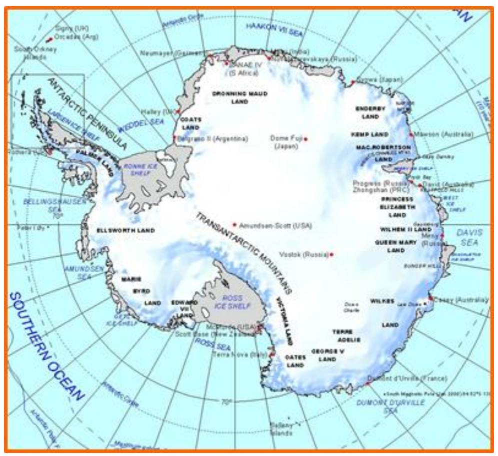
Why Antarctica?

Presently, more than 80 scientific stations located in Antarctica and more than 3000 people permanently living there as staff of the stations

Polymers are used as parts of buildings, vehicles, instruments, packaging and garments.

Specific environmental conditions:

- Extremely low temperatures
- Short diurnal period
- Long polar nights
- Short summer period



POLYMER FRIENDLY?

But: Existence of ozone depletion (ozone hole)
High and fast diurnal changes of temperature
Strong winds drifting ice crystals

Antarctic climate - how is the overall effect on polymer and its stability?
Up to 2019, no information on polymer environmental degradation in Antarctica was published in scientific literature (WOS, Scopus)

J.G.Mendel Polar Scientific Station

Located on James Ross Island in Antarctica (S 63°49´, W 57°53´)

Built and operated by Masaryk University Brno (Czech Republic) since 2005

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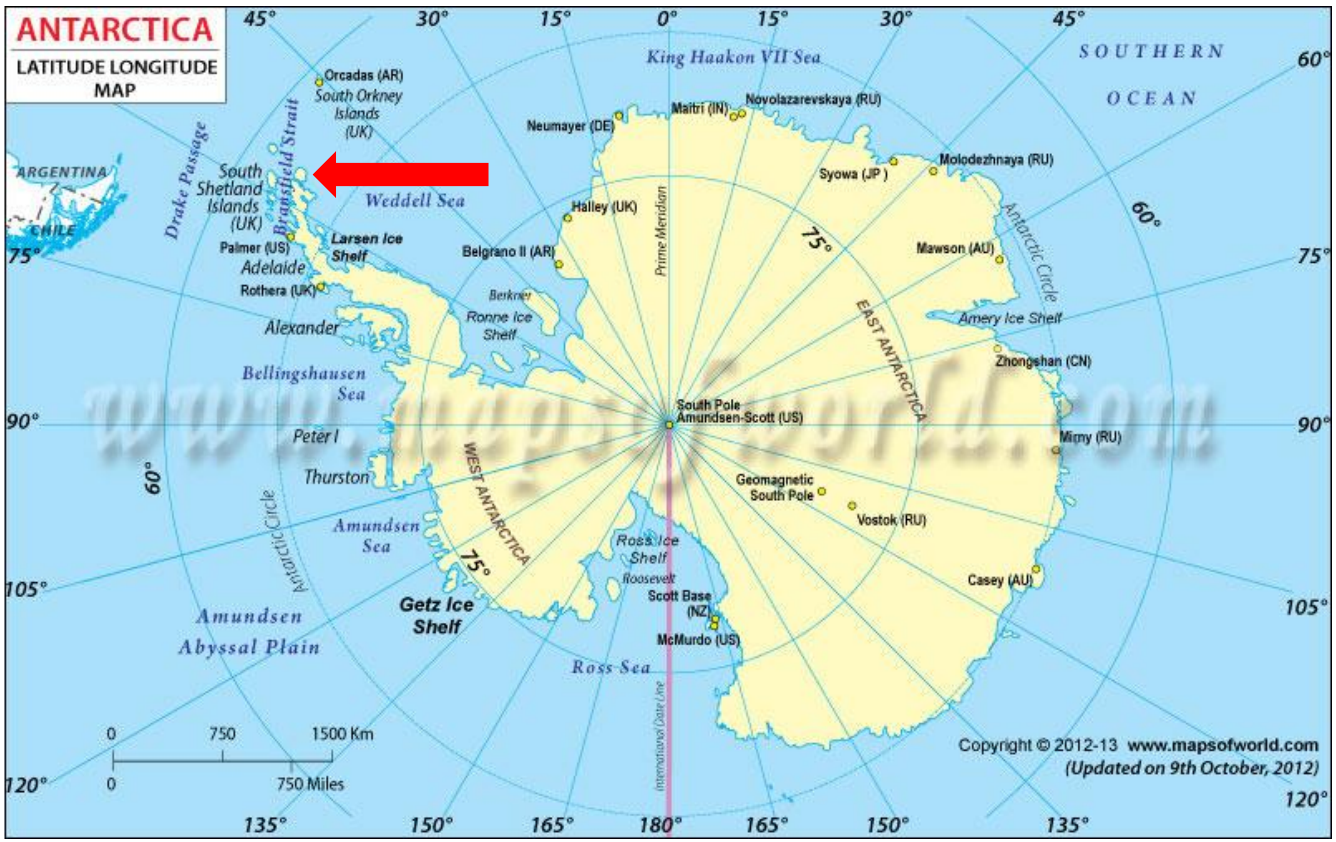
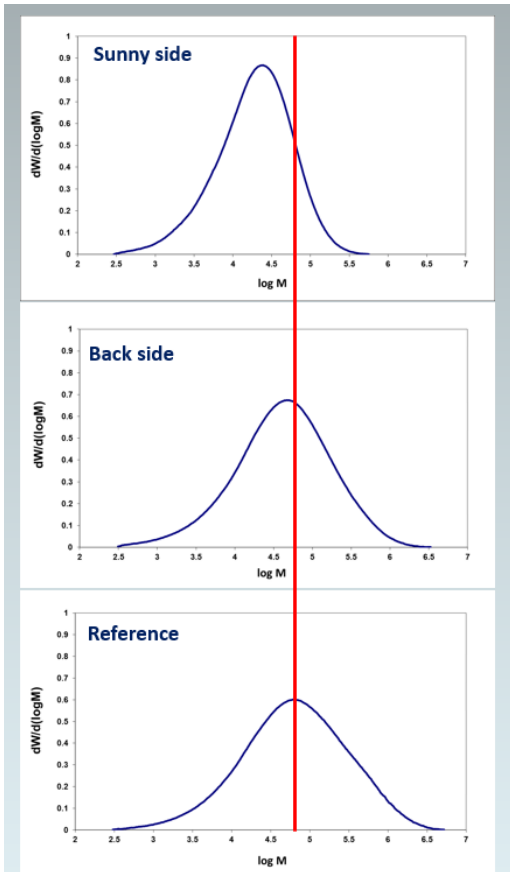


Environmental degradation in Antarctica

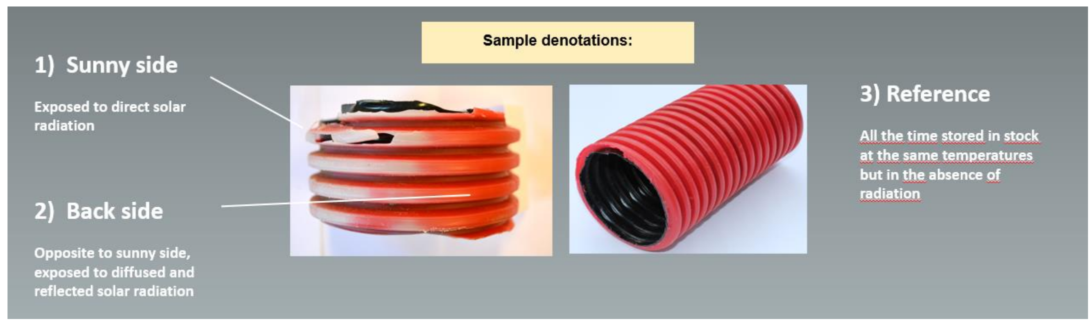
First observations (2014):



Molecular Weight Distribution (MWD)

High density polyethylene (HDPE) - extruded, corrugated pipe

Diameter:	110 mm
Wall thickness:	0.65 ± 0.05 mm
Stabilization:	Processing, no UV



The pipe was exposed 9 years outdoors in Antarctica on James Ross Island (S 63°49', W 57°53')

Serving as mechanical protection of electrical cabling installed between J.G. Mendel Station and its remote scientific facilities

Environmental degradation in Antarctica

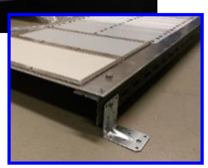
Long-term weathering experiment 2015-2020:

Materials: Polypropylene (PP) – <u>homopolymer</u> (random copolymer, impact copolymer)

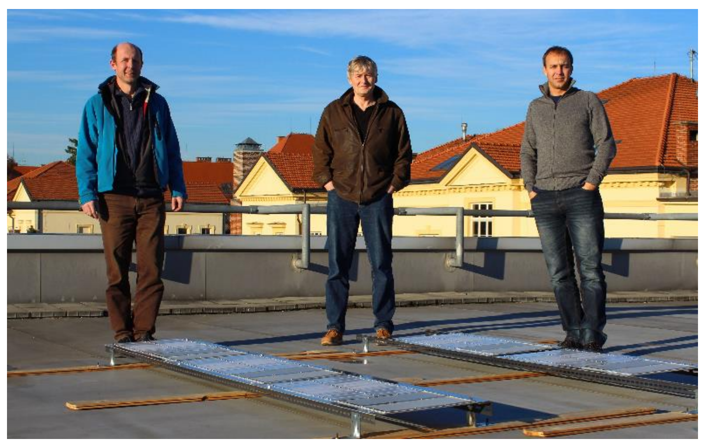
Exposure sites: a) James Ross Island (Antarctica)
b) Brno, Czech Republic (Central Europe)

Time-span: 5 years or + / sampling once a year

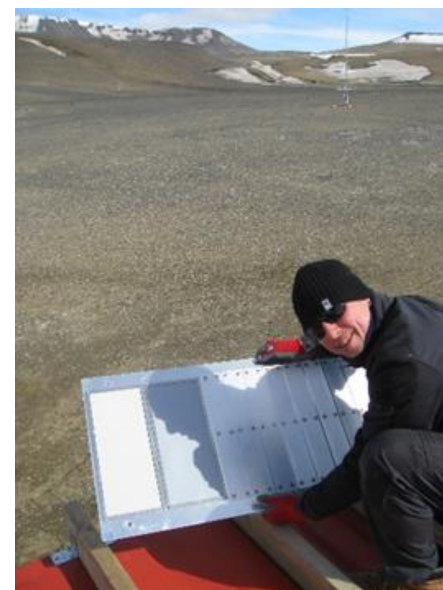
Aluminium carrier racks



Exposure site in Brno, CZ (Central EU)



Exposure site
James Ross Island (Antarctica)

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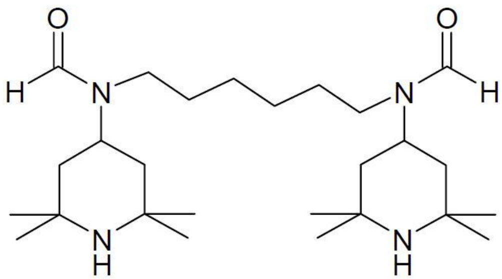
Třebíč
Jindřichův Hradec
České Budějovice
Uherské Hradiště
Znojmo
Břeclav
Český Krumlov
50° N
14° E
16° E
18° E
N
0 40 Miles
0 40 Kilometers
(C) ParsCom
BRNO
Reference exposure site

Environmental degradation in Antarctica

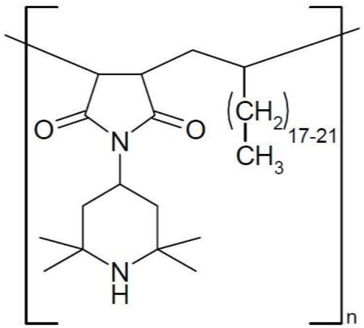
PP-homopolymer: Mosten (Unipetrol RPA), isotactic homopolymer, gas-phase process
MFI=3 dg/min. (230°C/2.16 kg; ISO 1133)

Sample geometry: Extruded sheets 0.5 mm thick (chill-roll technology)

Additivation (tailor-made): *Base*: 0.15% Irganox B225, 0.02% Ca-stearate SP, 0.02% Hycite 713
Light stabilization: a) *none*
b) 0.1% HALS-1
c) 0.1% HALS-2



HALS-1 (Uvinul 4050H)
UV stabilizer, low-molecular type
(CAS No. 124172-53-8; Mol. weight 450 g/mol)



HALS-2 (Uvinul 5050H)
UV stabilizer, oligomeric type
(CAS No. 152261-33-1; Mol. weight 3000-4000 g/mol)

Environmental conditions

Climatic conditions were continuously recorded at both exposure sites

Antarctica (JGM station) – overview of environmental data in the years 2015–2017.

Period	Months	T_{min} (°C)	T_{max} (°C)	T_{avg} (°C)	UV-A (MJ/m^2)	UV-B (MJ/m^2)	TUVR (MJ/m^2)	Global (MJ/m^2)	TOC (DU)
9.1.2015–6.2.2016	13	−11.0	−3.1	−7.2	297.8	5.5	303.3	4272.6	280.8
7.2.2016–21.1.2017	11	−8.4	−1.3	−5.1	214.1	3.4	217.5	3200.9	283.6
22.1.2017–19.1.2018	12	−11.1	−3.2	−7.3	268.6	4.4	273.0	3620.8	285.9
				Total:	780.5	13.3	793.8	11 094.3	283.4[a]

Brno (Czech Republic) – overview of environmental data in the years 2015–2017.

Period	Months	T_{min} (°C)	T_{max} (°C)	T_{avg} (°C)	UV-A (MJ/m^2)	UV-B (MJ/m^2)	TUVR (MJ/m^2)	Global (MJ/m^2)	TOC (DU)
13.1.2015–9.2.2016	13	6.1	14.9	10.5	287.5	4.6	292.2	4 305.7	330.4
10.2.2016–13.1.2017	11	6.5	15.7	11.1	255.8	4.6	260.3	4 013.2	322.3
14.1.2017–12.1.2018	12	6.3	15.5	10.9	273.7	5.0	278.7	4 360.2	320.4
				Total:	817.0	14.2	831.2	12 679.1	324.4[a]

T_{min} - average of daily minimum temperatures.
T_{max} - average of daily maximum temperatures.
T_{avg} - average of daily average temperatures.
[a] average value.

Incident solar radiation ranges:

UV-B	280-315 nm
UV-A	315-400 nm
Global	280-2800 nm
TUVR =	UV-A + UV-B

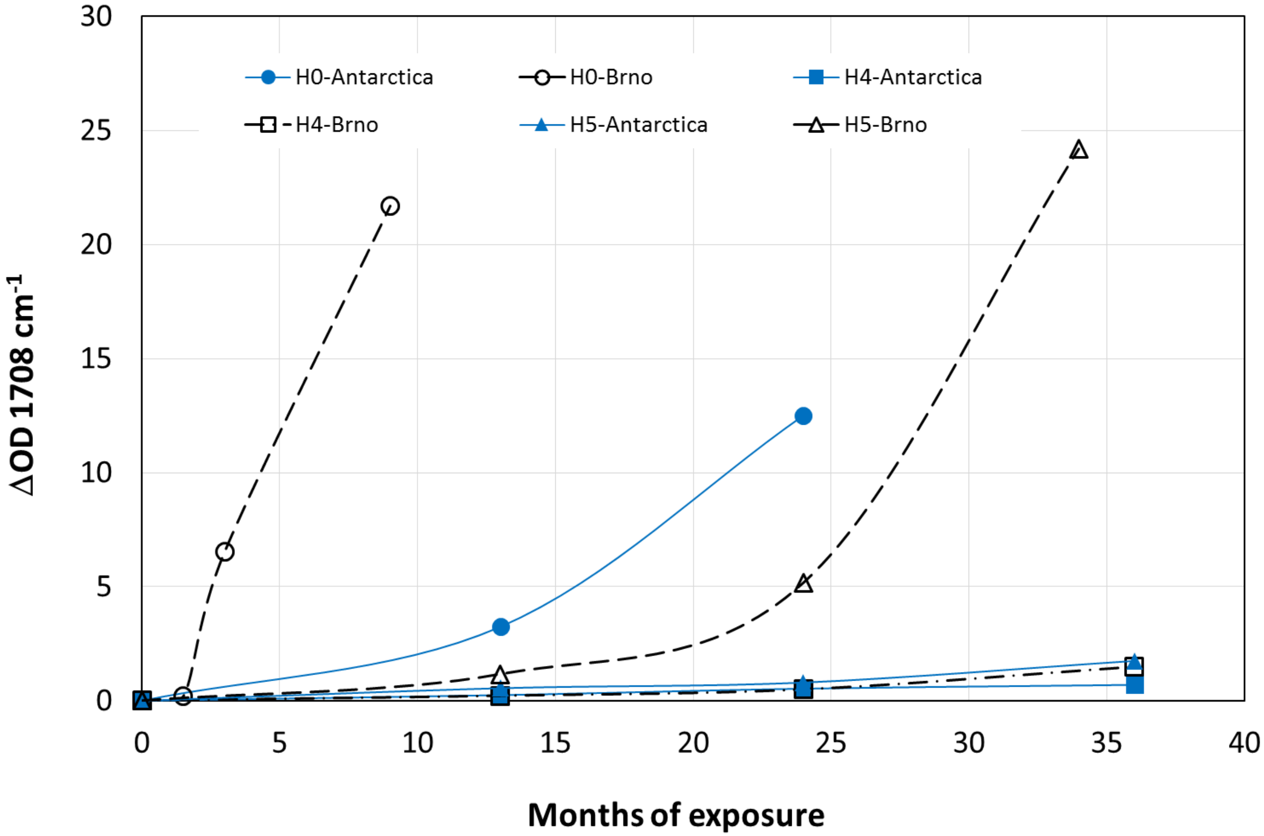
Radiation energy ratio:	Antarctica (%)	Brno (%)
UV-A / Global	7.0	6.4
UV-B / Global	0.12	0.11
TUVR / Global	7.2	6.6
UV-B / UV-A	1.7	1.73

Based on 3-year cummulative data

Environmental degradation in Antarctica

Carbonyl Index (CI) $CI = A_{1708} / A_{1892}$ *A_{1708}, A_{1892} …….. absorbances of carbonyls and reference band, respectively*

Optical density (OD) $\Delta OD = CI_t - CI_0$ *CI_t, CI_0 ……. carbonyl indices at time of sampling and before exposure, respectively*



Environmental degradation in Antarctica

Denotations of test specimens:

E.g. specimen **AH4-13**

A ... Antarctica
B … Brno

H …. homopolymer

0 … non UV-stabilized
4 … stabilized with HALS-1
5 … stabilized with HALS-2

Months of exposure

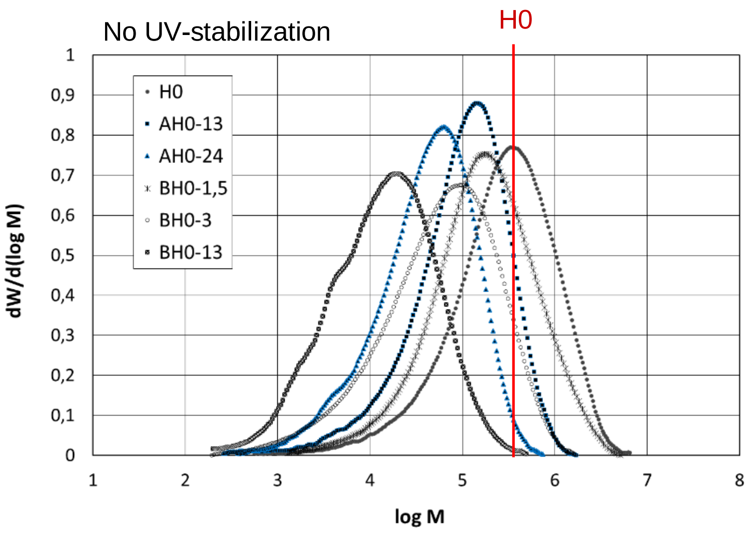
Denotations H0, H4 and H5 stand for the non-exposed polymers.

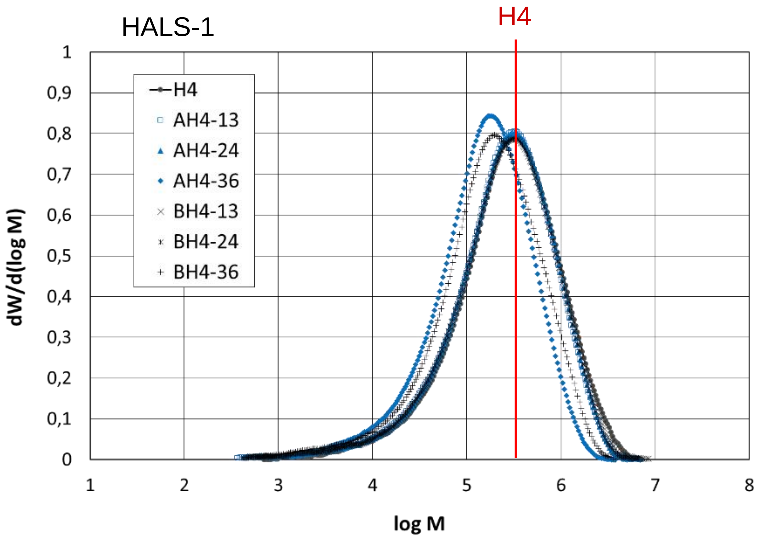
Molecular weight (GPC)

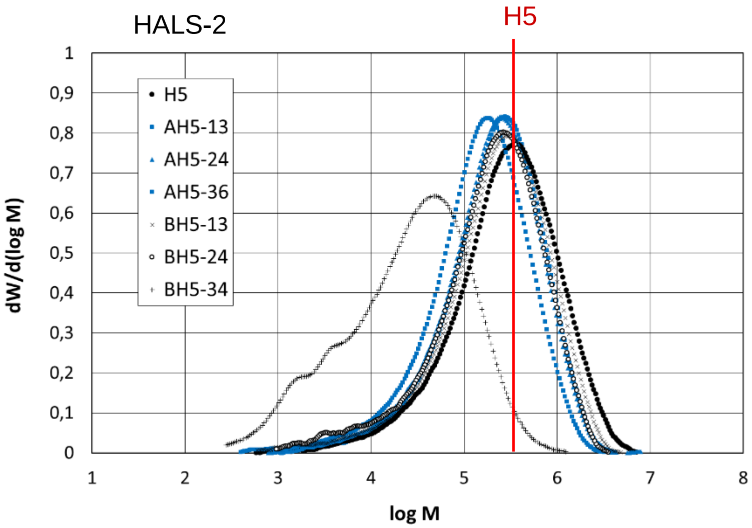
Average molecular weights in thousands g/mol and polydispersity

Sample	M_w	M_n	M_w/M_n
H0	527	75	7.0
H4	507	78	6.5
H5	535	75	7.1
AH0-13	162	32	5.1
AH0-24	70	14	5.0
BH0-1.5	344	60	5.8
BH0-3	126	15	8.3
BH0-9	26	5.8	4.5
BH0-13	28	5.3	5.3
AH4-13	440	55	8.0
AH4-24	446	55	8.2
AH4-36	255	44	5.9
BH4-13	469	56	8.4
BH4-24	451	51	8.9
BH4-36	319	42	7.6
AH5-13	367	72	5.1
AH5-24	344	68	5.1
AH5-36	258	41	6.3
BH5-13	419	51	8.2
BH5-24	356	47	7.6
BH5-34	60	6.6	9.1

Molecular weight (GPC)

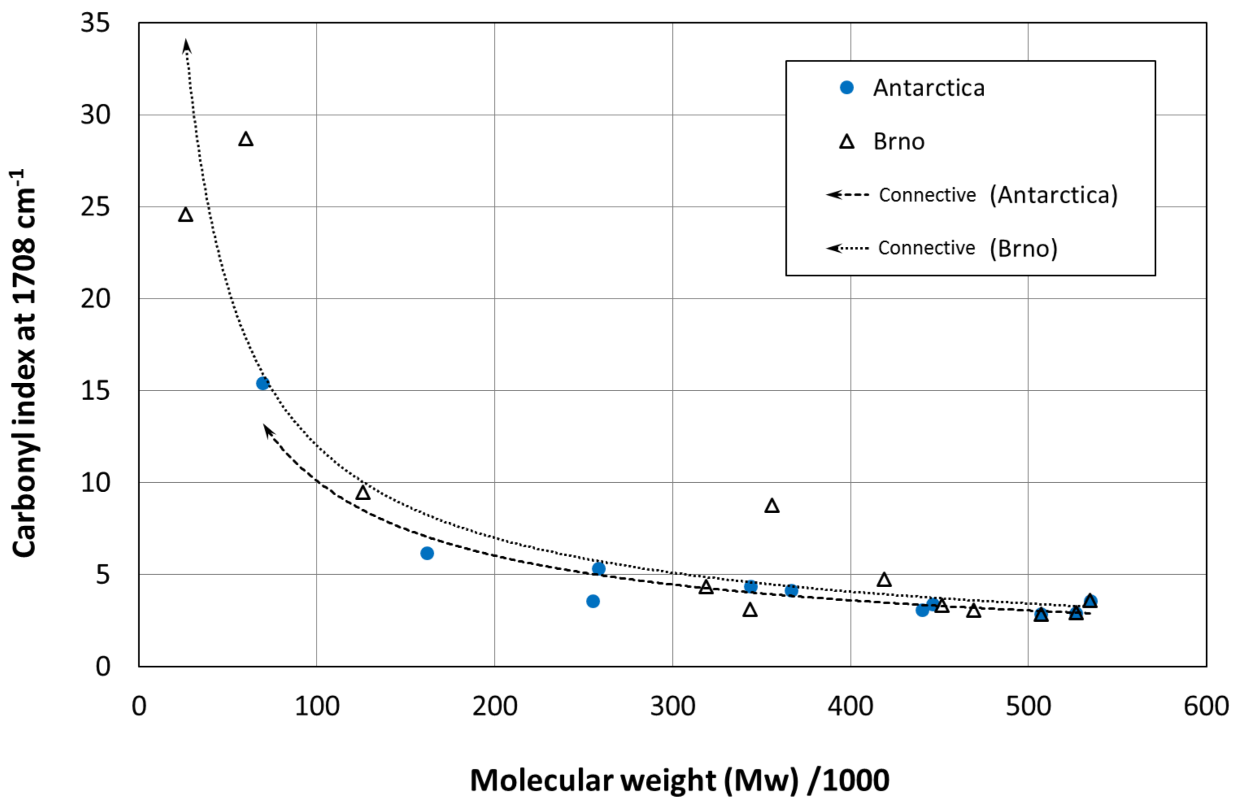






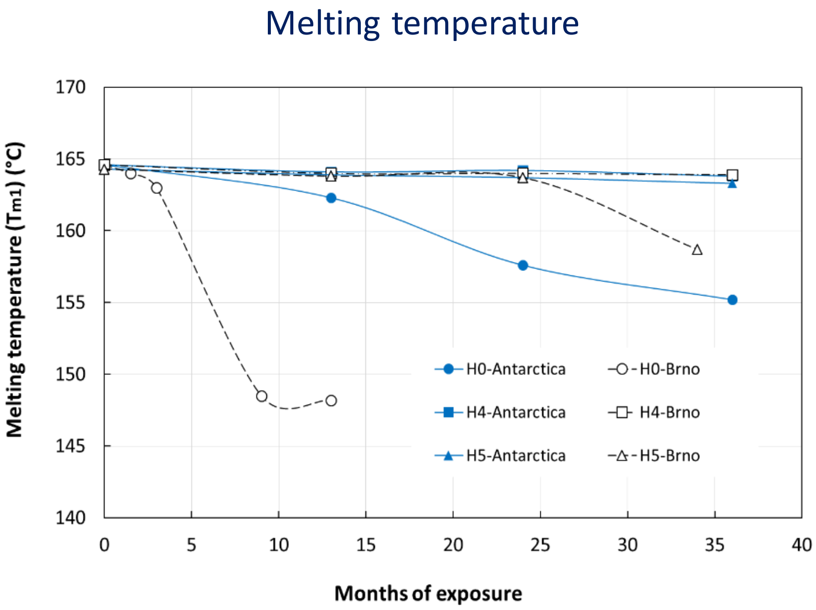
Environmental degradation in Antarctica

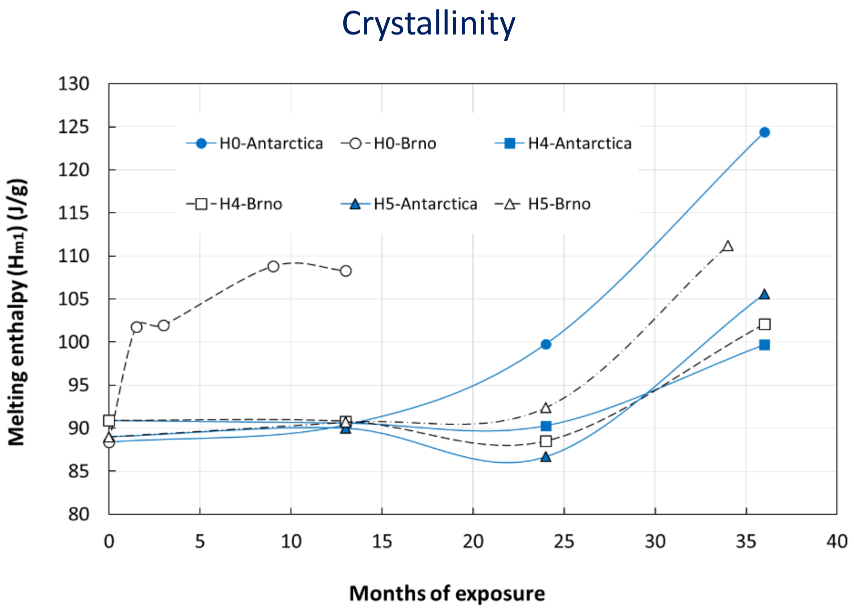
PP-homo: Intensive carbonyls formation mostly induced by dramatic drop in weight average molecular weight at both localities



Thermal analyses - DSC

PP-homopolymer:

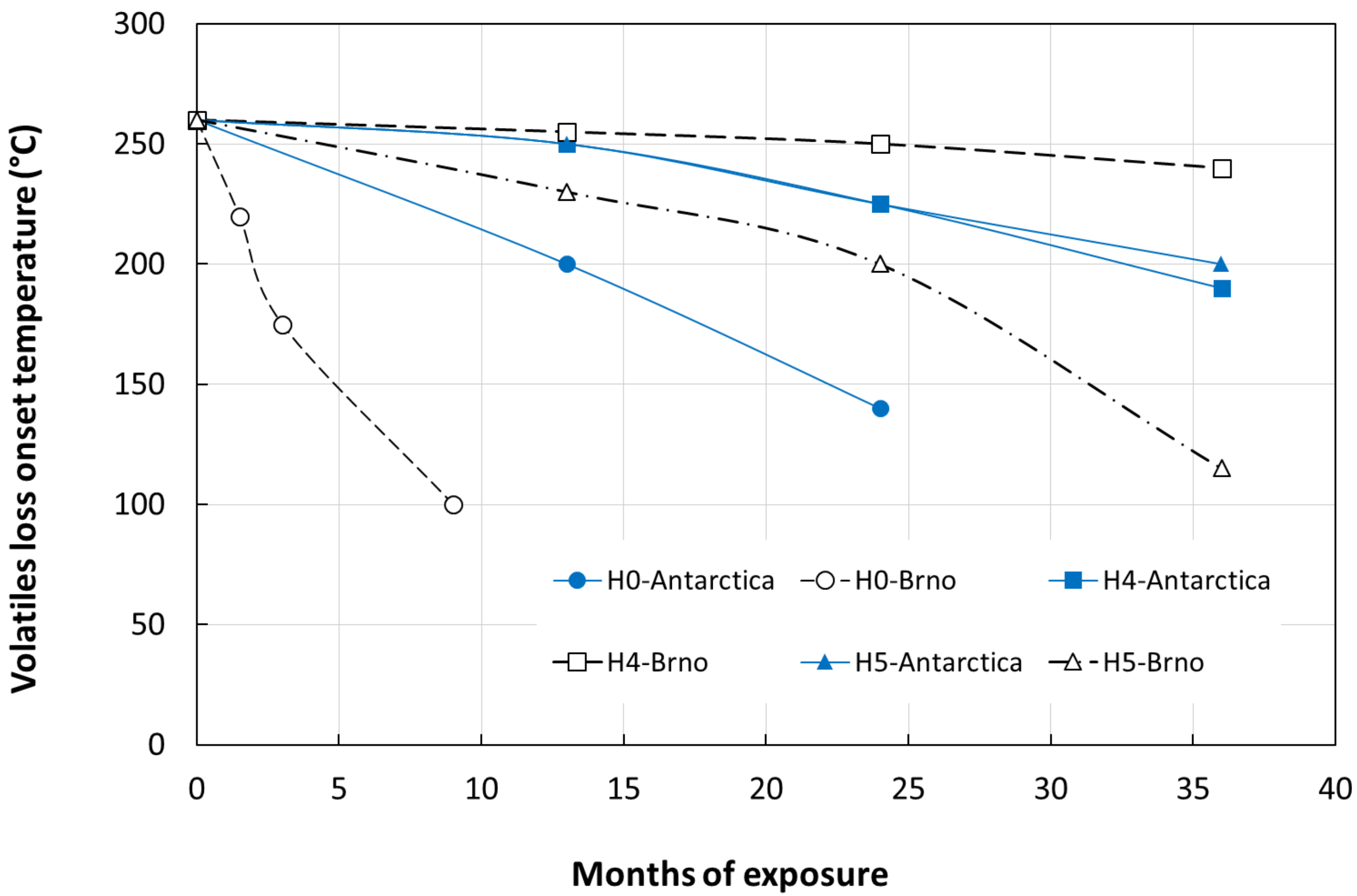




- **Proceeding degradation decreased the molecular weight – drop in melting temperature (T_{m1})**
- **Shorter macromolecules exhibiting better mobility lead to increased crystallinity (~H_{m1})**

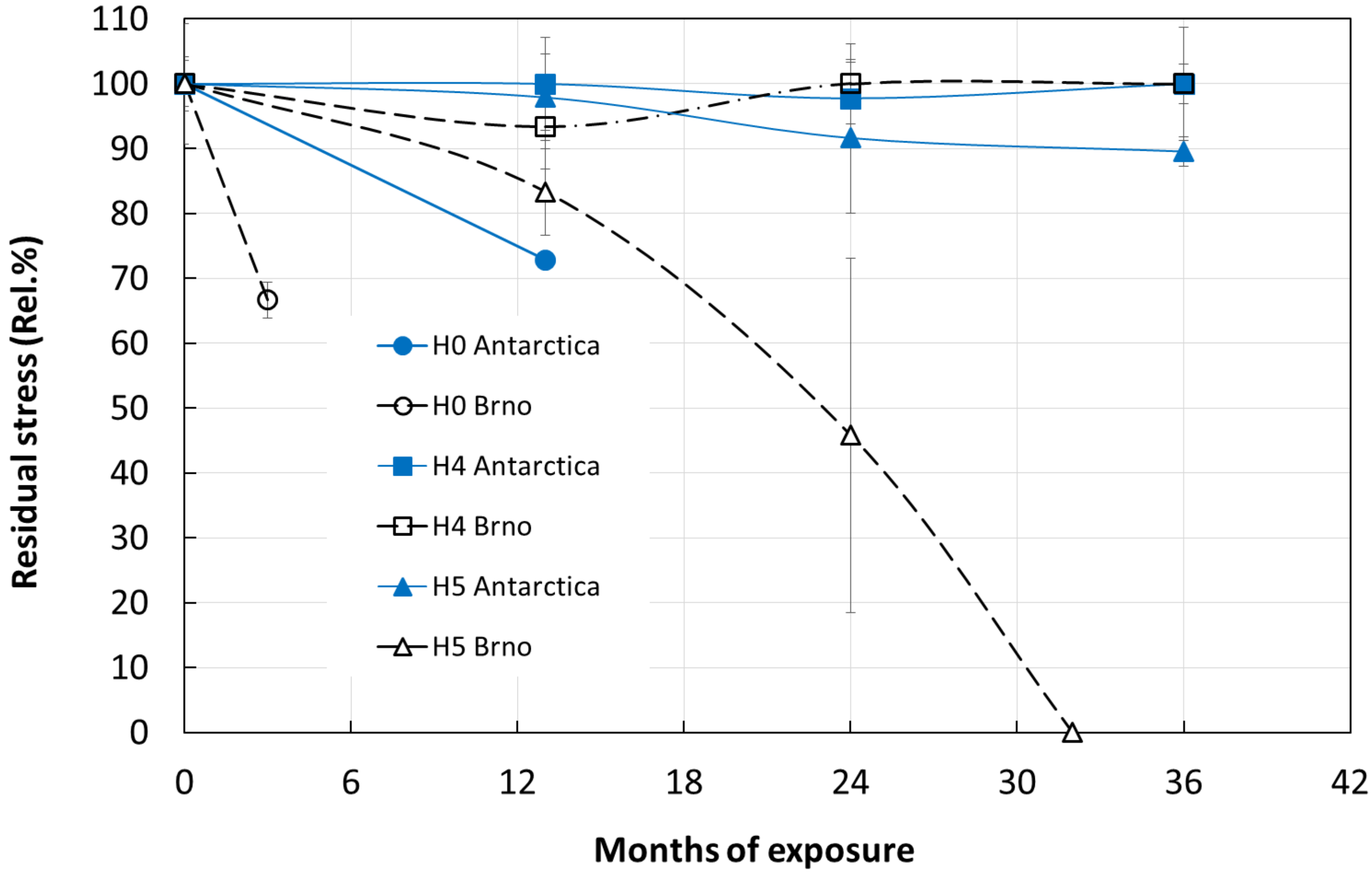
Thermogravimetric analysis (TGA)

Volatiles loss onset (VLO) – defined as temperature at which formation of volatiles exceeds 0.1 wt.%



Mechanical properties – tensile test

PP-homopolymer: 0.5 m film, dog-bone tensile test specimens, grip distance 50 mm, crosshead speed 50 mm/min.



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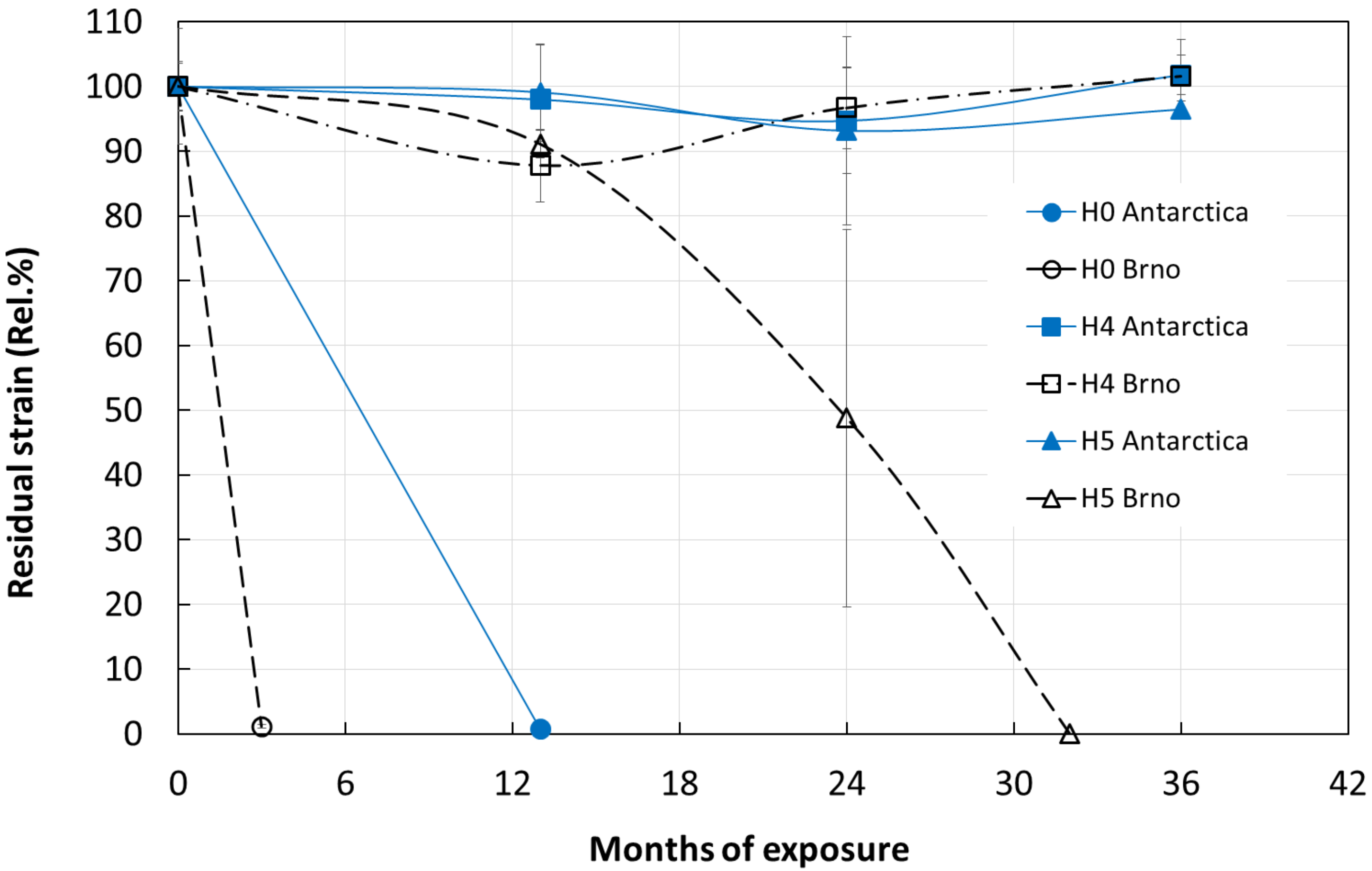
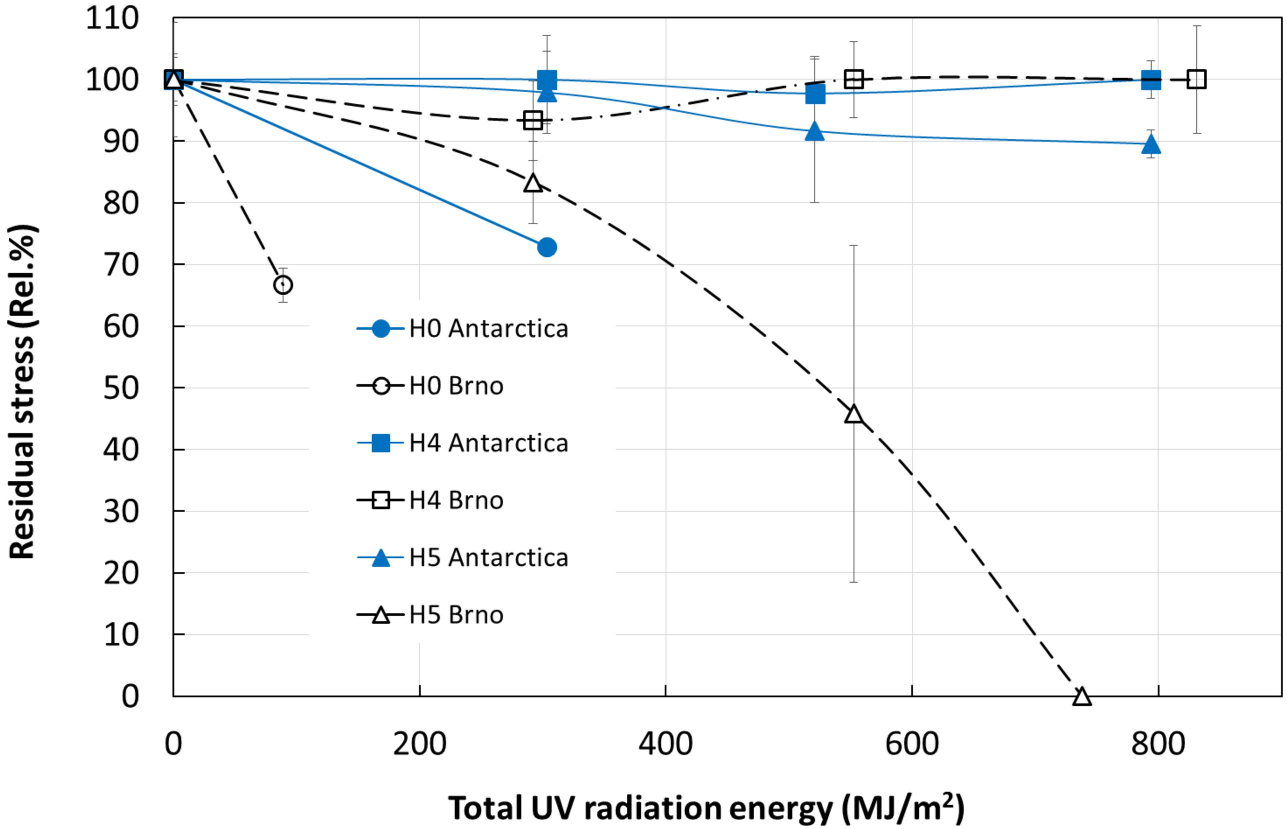


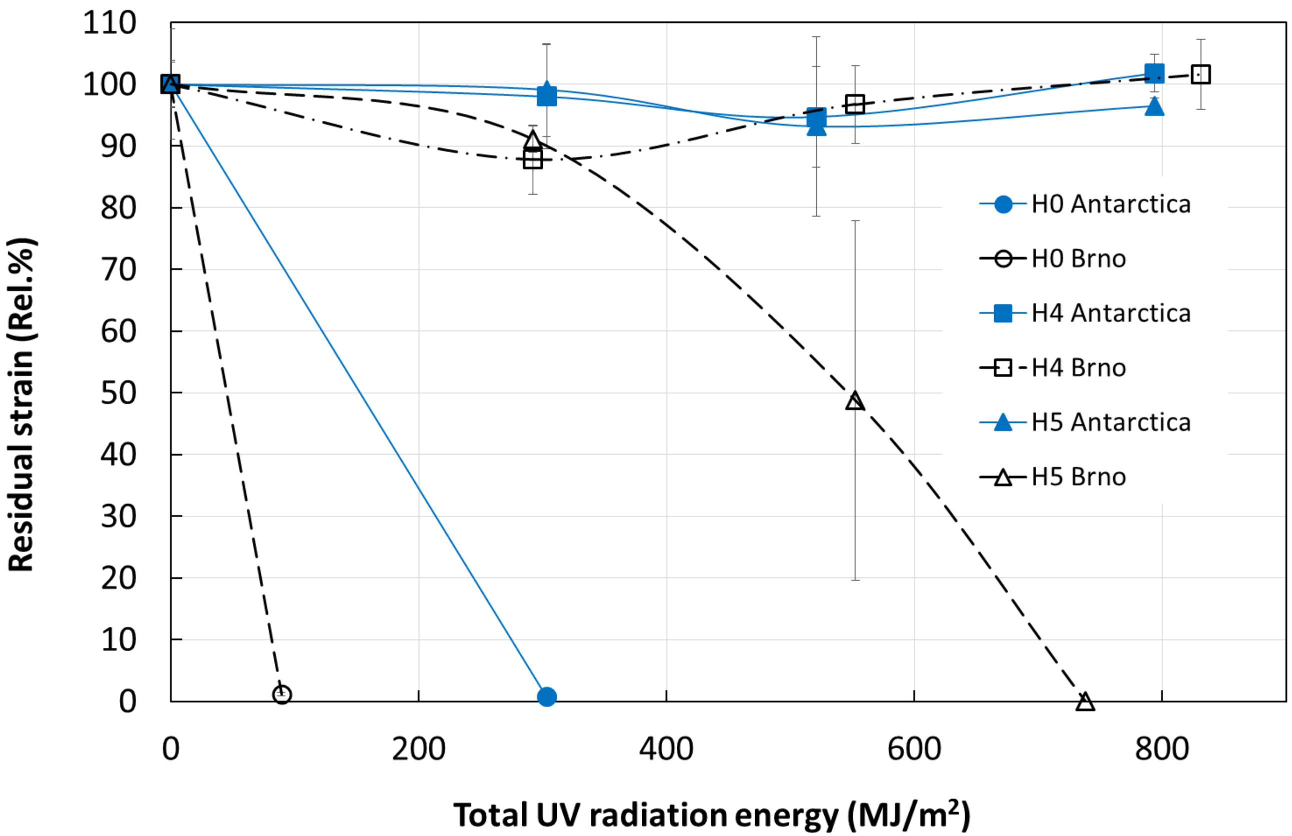
Mechanical properties vs. radiant energy

PP-homopolymer: 0.5 m film, dog-bone tensile test specimens, grip distance 50 mm, crosshead speed 50 mm/min.



Mechanical properties vs. radiant energy

PP-homopolymer: 0.5 m film, dog-bone tensile test specimens, grip distance 50 mm, crosshead speed 50 mm/min.

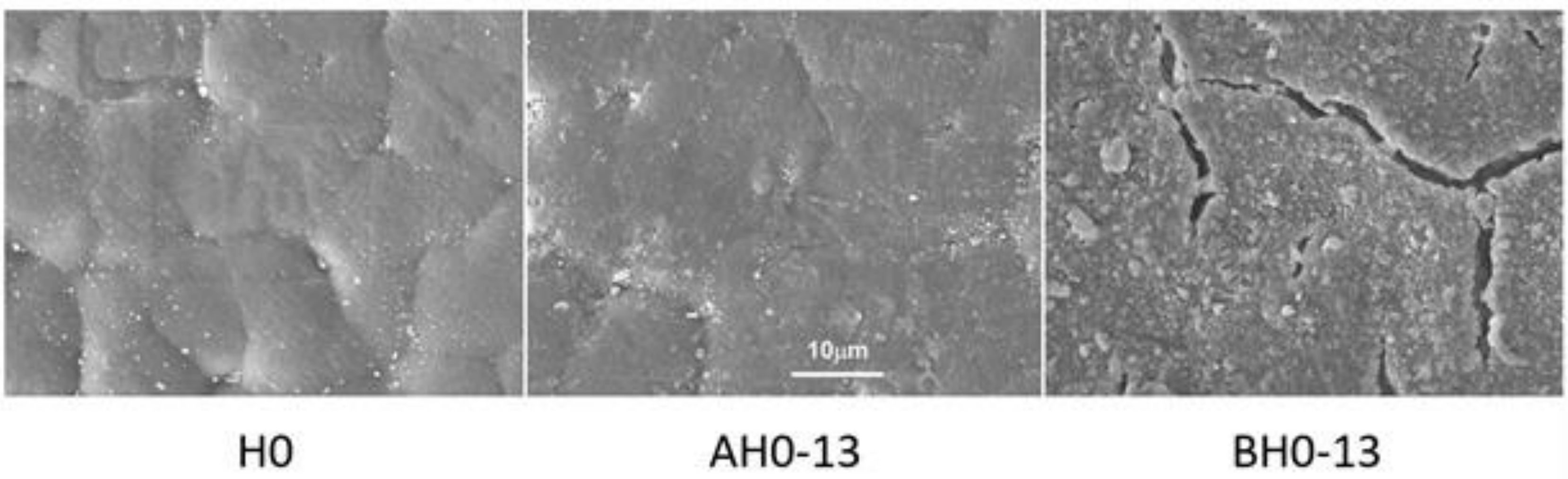


Surface morphology – SEM imaging / 13 months

Non-UV-stabilized polymer – surface deterioration after 13 months of outdoor exposure

Antarctica – minimum visually observable changes on the surface
Brno – total degradation of both surface/bulk

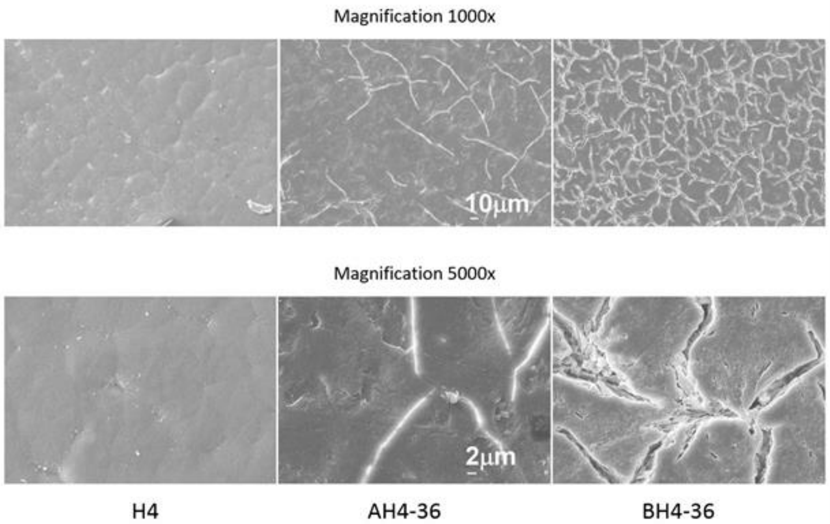
Magnification 10 000 x



Surface morphology - SEM imaging / 36 months

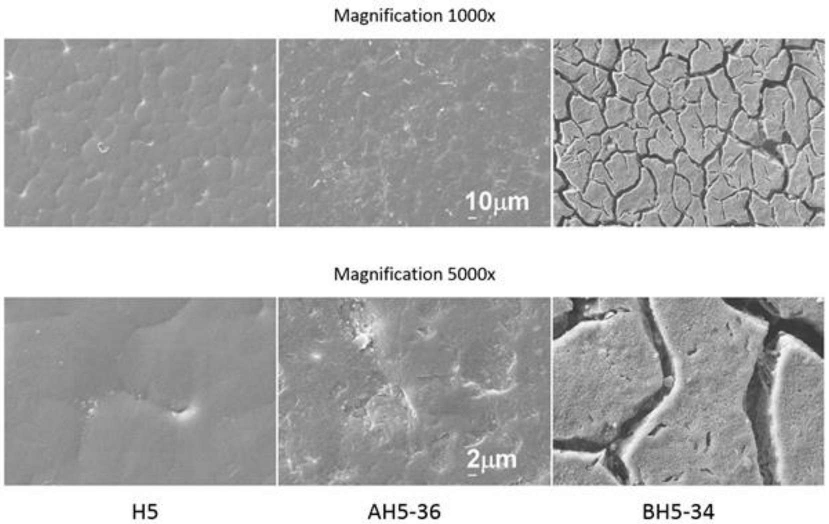
HALS-1
Mostly surface deterioration at both localities

Degradation allowed by extraction of low-molecular HALS from the surface layer of polymer



HALS-2
Slight surface degradation in Antarctica
Bulk degradation in Brno

Low stabilization efficiency of oligomeric HALS at higher ambient temperatures



Antarctica vs. Central Europe

Two principal factors controlling polymer degradation rate during outdoor exposure

1) Radiant energy:

	UV-A (MJ/m^2)		UV-B (MJ/m^2)		Global (MJ/m^2)	
Months:	**Antarctica**	**Brno**	**Antarctica**	**Brno**	**Antarctica**	**Brno**
0	0	0	0	0	0	0
13	297.8	287.5	5.5	4.6	4272.6	4305.7
24	511.9	543.3	8.9	9.2	7473.5	8318.9
36	780.5	817	13.3	14.2	11094.3	12679.1

Radiation energy ratio:	Antarctica (%)	Brno (%)
UV-A / Global	7.0	6.4
UV-B / Global	0.12	0.11
TUVR / Global	7.2	6.6
UV-B / UV-A	1.7	1.73

Higher overal radiant dose in Brno (CE)

More TUVR in global radiation in Antarctica

Cumulative data on radiation energy incident on tested materials during the experiment

2) Temperature:

Average ambient at the exposure sites

Antarctica: - 6.5 °C

Brno (CZ): 10.8 °C

Δ = ~ 17 °C

Kinetics

Estimation of polymer service-life based on mechanical properties:

	Months	Property dropped by 50%
H0-Antarctica	6	strain
H0-Brno	1.5	strain
H4-Antarctica	> 36	n.a.
H4-Brno	> 36	n.a.
H5-Antarctica	> 36	n.a.
H5-Brno	23	stress

4 x

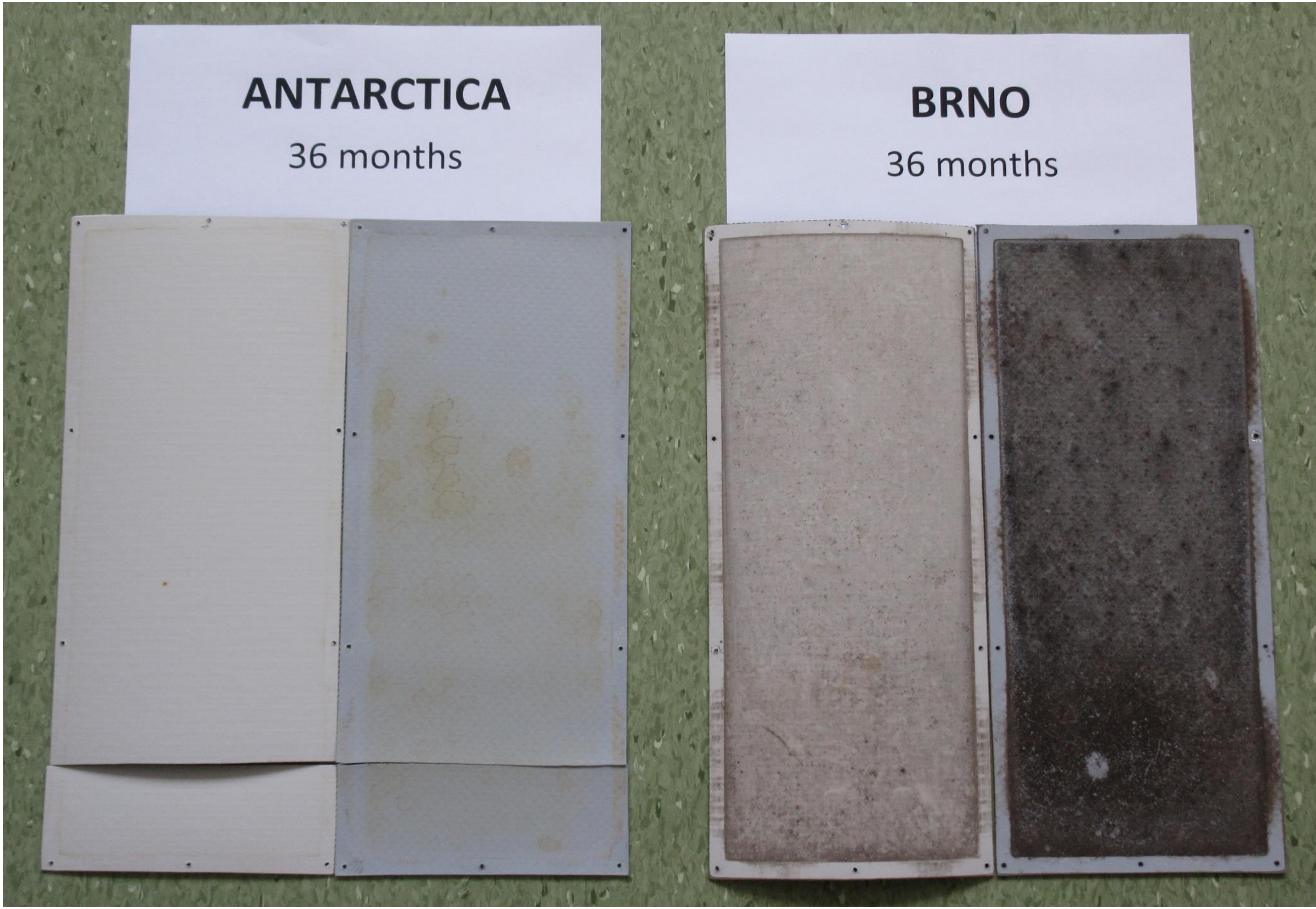
If weathering was controlled only by temperature:

$$\ln k_2/k_1 = -E_a/R\ (1/T_2 - 1/T_1)$$

k_2/k_1= **2.8**

$k_{2,}$ k_1 ….. rate constants in Brno and Antarctica, respectively
E_a …..... activation energy (37.9 kJ/mol)
R …..... gas constant (8.314 J/°K/mol)
$T_{2,}$ T_1 …. absolute temperatures in Brno and Antarctica, respectively

OVERALL: In Antarctica degradation is mostly controlled by solar radiation, while temperature plays only marginal role
In Brno degradation is controlled both by solar radiation and temperature



Airborne pollutions demonstrated on roofing materials tested together with PP

Conclusions:

- **Antarctica´s environmental conditions seem to be at first sight polymer friendly but even here synthetic polymers degrade**
- **Antarctic climatic conditions are characterized by very low ambient temperatures and a higher portion of TUVR in the global radiation as a consequence of ozone hole. Both compared to Central Europe (CE)**
- **Environmental degradation of PP-homopolymer was found to be faster in CE, the difference, however, was lower than we expected before starting this experiment**
- **Higher degradation rate in CE may be accounted for the higher absolute yearly dose of radiant energy and higher ambient temperatures. Airborne pollutions in CE may also have contributed**
- **Efficient UV stabilization of polypropylene against Antarctic climatic conditions with both low-molecular and oligomeric HALS stabilizers is possible**

Even in Antarctica synthetic polymers degrade,

compared to Central Europe at a slower rate but definitely not negligibly !

Thank you for your attention !