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Antarctica – A unique location for the testing of polymers

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Abstract

The Johann Gregor Mendel Czech Antarctic Station (JGM), located in the northern part of James Ross Island in Antarctica, provides a facility for research in many scientific disciplines, such as geography, geology, climatology and biology. In 2015 its activities were extended by the testing of plastics. When synthetic polymers, often referred to as plastics, are exposed to outdoor conditions they undergo irreversible changes due to the absorption of incident solar UV radiation and the consequent reactions with oxygen. Their stability and reliability for outdoor applications are tested through weathering at various locations around the world. Until 2015, when systematic research into plastics started at the JGM, no information on the resistance of plastics to the Antarctic climate was available.

Key words: weathering, plastics, polymers, degradation, outdoor exposure, Antarctica

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Abbreviations: JGM – Johann Gregor Mendel station, HDPE – high-density polyethylene, *h*-PP – polypropylene homopolymer, *ic*-PP – polypropylene impact copolymer, MFR – melt-flow rate, UV-A – radiation in 315–400 nm range, UV-B – radiation in 280–315 nm range, TUVR – total UV radiation (290–400 nm), M_w –weight average molecular weight, M_n – number average molecular weight, MWD – molecular weights distribution, HALS – hindered-amine light stabilizer

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Introduction

The Czech scientific station J.G. Mendel, located in the northern part of James Ross Island, went into operation in 2007. Since then, it has been used by various teams of experts from a wide range of natural sciences, such as geology, geomorphology, climatology, plant biology, microbiology and many others (Prošek et al. 2013). In 2015, the research portfolio was extended by the investigation of plastics and in particular, structural changes they might undergo due to exposure to the Antarctic environment.

Prediction of the service life of plastics

To learn how polymers behave when applied in a particular application under real conditions, accelerated testing is often adopted. This involves the irradiation of a sample using an artificial laboratory light source that features: (1) the specific spectral power distribution (especially the range of the UV light) and (2) the higher level of radiation intensity. Although this approach provides some preliminary information on the UV stability of a polymer in a relatively short period of time, it has its drawbacks. Laboratory light sources, despite suitable filtration, are still not able to fully mimic the spectral distribution of the incident solar radiation. Additionally, accelerated tests are frequently carried out at elevated temperatures that control the reaction kinetics and increase the rate of polymer degradation (Audouin et al. 1998, Pickett et al. 2008, Tocháček et al. 2014).

Accelerated testing that uses high irradiation levels and higher temperatures produce problems in the extrapolation of the results, *i.e.*, the faster the polymer is aged, the higher the lack of certainty in the results of the extrapolation (Brown 1999, Tocháček et al. 2014). If there is no need for rapid results, weathering tests are performed. The exposure of a polymer to real outdoor environmental conditions provides the most objective information on its UV stability in that specific climate at that particular location. The only disadvantage of this approach is that it takes considerably longer than laboratory tests. Long-term outdoor exposure allows the natural diffusion of oxygen into the polymer and the simultaneous effect of the ambient temperature at which degradation reactions take place. Therefore, there is no further extrapolation required in this type of testing. Although weathering tests may be carried anywhere around the world, there are two pilot exposure locations, with elevated annual radiation doses that are commonly recognized (Weathering Testing Guidebook, 2001[1], *see* Table 1):

	Annual radiant exposure*	**Mean humidity**	**Type of climate**
Florida (US)	6 500 MJ/m^2	78 %	Maritime, wet
Arizona (US)	8 000 MJ/m^2	37 %	Continental, dry

Table 1. Annual radiation doses incident on two reference plots (Adopted from Weathering Testing Guidebook, 2001[1]). *Note*: *Global solar radiation between 295-3000 nm.

These locations are the best known and most popular because they expose the samples to a high intensity of solar radiation throughout the year and allow the polymer weathering tests to be concluded relatively quickly. They serve as a benchmark for the weathering of polymers. In addition, there are many other locations where polymers may be exposed to the specific conditions of the individual localities (Wypych 2013). However, until 2015, polymer weathering data for Antarctic climatic conditions was missing.

How did it all begin – Why Antarctica?

The primary impulse came in 2014. Lukáš Krmíček, who was a member of the Antarctic expedition from Masaryk University, recognized that some of the plastics, used as part of the outdoor cable protection, had visibly changed colour after some years of outdoor exposure. He collected samples and took them back to Brno to the specialist laboratory at the Central European Institute of Technology (CEITEC) that was working on the degradation and stability of polymers. Analyses of the materials confirmed his preliminary visual observations and provided evidence of a high degree of oxidative degradation. Until that time, no information had been published on the outdoor exposure of polymeric materials in Antarctica. This lack of information on the effect of the Antarctic climate on polymers stimulated research in this area. On one hand it seemed that the Antarctic climate should be very gentle on polymers due to its extremely low temperatures, short diurnal period and unpolluted atmosphere. On the other hand, the detrimental effect of the hole in the ozone layer means that the shorter wavelengths of solar UV radiation are not filtered out (Láska et al. 2010). There is also a greater mechanical stress due to strong winds (Kavan et al. 2018). These have a mechanical impact on plastics and are the main factors that cause the Antarctic climate to have a very specific effect. Until we generated our own research results, no one could say with certainty, what the overall effect of these simultaneous factors might be. This was what made the long-term testing of plastics in Antarctica so interesting and gave rise to the idea that systematic research into plastics stability under these unique and very specific climatic conditions was needed.

The study site was the J.G. Mendel station located in the largest ice-free area in the Antarctic Peninsula region (Kavan et al. 2017), on the border of the oceanic and continental climate zones (King et al. 1994). Compared to the western, more humid side of the Antarctic Peninsula, the J.G. Mendel station has a drier and colder climate, from 2011 to 2021 the mean annual air temperature was -6.7°C (Kaplan-Pastíriková et al. 2023), the daily mean summer temperature was between -5° and 8°C (Láska et al. 2011) with gusts of wind that exceeded 20 $m.s^{-1}$ (Kavan et al. 2018). Another feature of the Antarctic climate is the extensive ozone depletion area (Farman et al. 1985, Solomon 1999), which forms over the continent each spring (August-October) and plays an important role in increasing the levels of UV irradiation in the coastal region (Petkov et al. 2016). The highest UV radiation intensities in this region can be found during the second half of November or the beginning of December when the edge of the stratospheric polar vortex is often asymmetrically positioned in respect to the South Pole (Hassler et al. 2011, Čížková et al. 2023). This results in extremely low levels of ozone over the Antarctic Peninsula which causes very high levels of irradiation at the coastal stations, *e.g.*, J.G. Mendel, Marambio, and Palmer (Láska et at. 2010, Aun et al. 2020, Bernhard and Stierle 2020).

As an example of the energy flux variation at the JGM station, over the three-year experiment (2015–2017) the mean annual sum of the total UV radiation was 264.6 $MJ{\cdot}m^{-2}$, this was within both the UVA (260.2 $MJ{\cdot}m^{-2}$) and UVB (4.4 $MJ{\cdot}m^{-2}$) spectral ranges (Tocháček et al. 2019). A comparison of the radiant energies during this period confirmed that the ratio of UV-B to UV-A is almost unchanged, *i.e.*, it is not significantly influenced by the sudden reduction in the stratospheric ozone content during the spring months. The mean annual total of global solar radiation (2015–2017) was 3698.1 MJ·m^{-2}, with a typical seasonal variation, depending on solar elevation, of < 5 W·m^{-2} (July) to approximately ~350 W·m^{-2} close to the summer solstice (December). The mean air temperature measured for the period of the experiment was -6.5°C, with a daily mean minimum temperature of -11.1°C and a daily mean maximum temperature of -1.3°C (Tocháček et al. 2019).

Material and Methods

HDPE corrugated pipe

It was the macroscopically degraded polymeric material that kicked-off our plastics-testing activity. Red corrugated plastics pipes were used outdoors as cable protection for the cables that connect the remote scientific instruments to the JGM station main building. One of these pipes, sampled by Krmíček in 2014, was seen to be visibly whiter than expected and this caught our attention. Although the pipe was a commercial product and we had no information on its composition, the matrix of the outer red shell was identified as high-density polyethylene (HDPE). Fortunately, we had information on the date of its installation outdoors plus we also had a reference sample. This was the same material, but it had not been used outdoors as it had been stored within the JGM facility in the absence of light and at the same temperature as the outdoor pipe.

Changes in the distribution of the molecular weight were determined through gel-permeation chromatography (GPC) which allowed us to explain, in detail, the changes that had taken place in the polymer.

Polypropylene materials

In the systematic long-term experiment mentioned in the earlier study (Tocháček et. al. 2019), polypropylene homopolymer (*h*-PP) materials were investigated. BERA Gravel Fix^{TM} sheet – a commercial product, the preliminary results of which are presented, is manufactured from a polypropylene impact-copolymer (*ic*-PP). Two identical sample *ic*-PP sheets were exposed to the outdoor conditions for a period of 13 months, one at the J. G. Mendel station (Antarctica) and the other in Brno, Kotlářská (Czech Republic, Central Europe). A further sheet was stored in Brno, without outdoor exposure, as a reference. These materials include a standard UV protection system based on hindered-amine light stabilizers (HALS).

Oxidation changes were investigated using FTIR spectroscopy in transmission mode, paying special attention to the wavenumber interval of 1700-1750 cm^{-1}, where carbonyls as the products of polymer oxidation absorb. Crystallinity was determined using differential scanning calorimetry (DSC) and melt-flow rates were determined using a Dynisco LMI 5000 melt-indexer at 230°C/2.16 kg.

Results and Discussion

Our investigation into the environmental stability of polymers in Antarctica can best be demonstrated by the following examples:

HDPE corrugated pipe

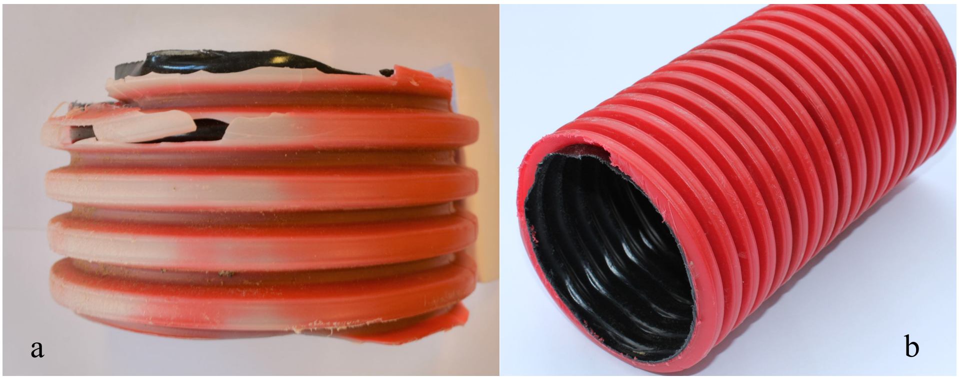

Fig. 1. Corrugated pipe (HDPE) – a) after 9-year exposure in Antarctica (left: directly irradiated side, right: back side exposed only to reflected radiation), b) non-exposed reference stored at dark place at the same temperature for the same period.

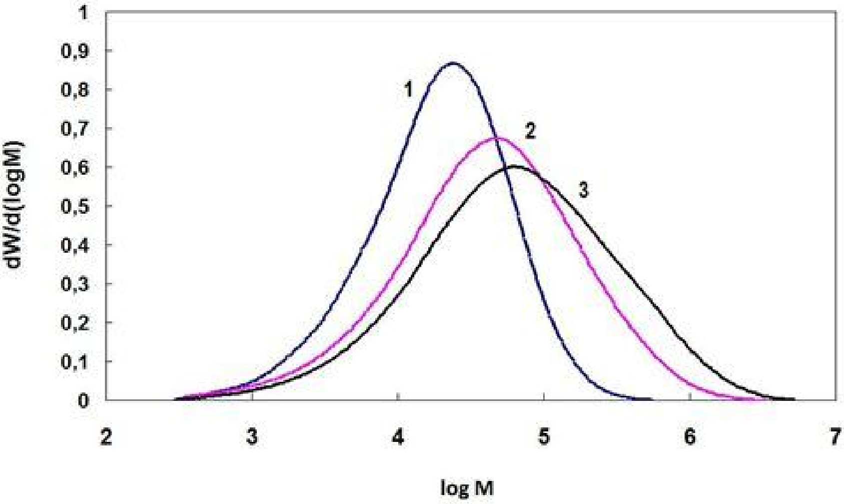

Fig. 2. Corrugated pipe (HDPE) – distribution of molecular weight (MWD) after 9-year exposure in Antarctica. 1 – irradiated side, 2 – back side, 3 – non-exposed reference.

Sample	**M_n**	**M_w**	**M_z**	**M_w/M_n**	**Inner viscosity** (dl/g)[GPC]
Irradiated side	9 000	32 200	76 600	3.58	0.5959
Back side	13 000	102 000	410 000	7.85	1.3155
Non-exposed reference	17 700	180 900	790 300	10.21	1.8525

Table 2. Corrugated pipe (HDPE) – average molecular weights after 9-year exposure in Antarctica (M_w - weight average molecular weight, M_n - number average molecular weight).

The GPC data supported the visual observations and confirmed that the visible changes in colour were associated with a strong reduction in molecular weight, both number and mass. The maxima of the molecular weights were shifted down and the dispersity of molecular weights (M_w/M_n) was considerably lower on the side exposed to UV radiation. All these changes indicate that strong oxidation took place and resulted in the dramatic scission of polymer chains, which consequently had a negative effect on the mechanical properties (the samples became brittle). These results convinced us that testing exposure in Antarctica makes sense and can provide measurable and interesting results.

PP homopolymer – a systematic project

The convincing results that came from the study of HDPE pipes made us realize that an extended scientific project, a comparison of the outdoor degradation rate in Antarctica versus Central Europe (Brno, Czech Republic), where our home universities are located, might provide some interesting results. We decided to use polypropylene (PP) for our systematic investigation due to its higher sensitivity to oxidation and the fact that its degradation is not complicated by crosslinking and is exclusively due to chain scission. The results of the first 3 years of this long-term experiment were published in Polymer Testing (Tocháček et al. 2019).

The findings answered some open questions and showed that despite the specific Antarctic environmental conditions, the *h*-PP degradation rate in Antarctica was still lower than that in Central Europe. Beside the UV radiation levels, the higher ambient temperatures that accelerate the secondary propagation reactions of alkyperoxy radicals were mainly responsible for the more rapid photo-induced degradation in Central Europe (Tocháček et al. 2019).

PP copolymer BERA Gravel Fix^{TM} - A ČEGAN utility product

In addition to the specifically prepared scientific test materials, commercial end products are also tested. The exposure of injection moulded polypropylene gravel stabilization sheet (Fig. 3) may serve as a case study. The results after the first year of exposure are as follows:

Fig. 3. BERA Gravel Fix^{TM} – a reference gravel stabilization sheet; non-exposed.

	Antarctica, JGM	**Central Europe, Brno**
Period of exposure	4.1.2022 – 4.2.2023	4.1.2022 – 7.2.2023
Exposure in days	396	399

Table 3. Timing of gravel fix sheets outdoor exposure.

	Antarctica JGM	**Central Europe Brno**	**Non-exposed reference**
Carbonyls at 1700-1720 cm^{-1} based on FTIR spectrum	not found	not found	not found
Carbonyl index (CI) at 1737 cm^{-1} based on FTIR spectrum*	3.0	2.4	3.0
Crystallinity by H_m (J/g) based on DSC analysis (1st melting)	106.5	102.7	99.3
Melt-flow rate (230°C/2.16kg) (dg/min.)	21.8 $\pm$ 1.5	23.8 $\pm$ 0.4	18.2 $\pm$ 0.3

Table 4. Properties of gravel fix sheets (PP-copolymer) after 13 months of exposure. *Note*: *FTIR spectra were measured in the transmission mode; carbonyl index (CI) at 1737 cm^{-1} was calculated as CI = A_{1737} / A_{1894}, where A were absorbances at 1737 and 1894 cm^{-1}, respectively. Absorbance at 1894 cm^{-1} served as an inner reference.

The FTIR spectra show that no carbonyls were found between 1700-1720 cm^{-1} that could have been accounted for by oxidative degradation. Carbonyls found at 1737 cm^{-1} belong to the ester functionality of the low-molecular HALS which are used as a component of the UV protection system (confirmed by the unexposed reference sample). Thus, CI at 1737 cm^{-1} indicates the physical presence of the stabilizer in the polymer. Some decrease in CI, after exposure in Brno, most likely indicates a partial physical loss of the stabilizer, due to more frequent rainfalls and higher average temperatures.

Although no oxidation of the polymer was found (absence of carbonyls at 1700-1720 cm^{-1}), some minor changes, due to weathering, were found. A partial increase in crystallinity and melt-flow rate, when compared to the reference, were found in both the Antarctica and Brno samples. Both analytical tests are, however, thermal and carried out at elevated temperatures. Higher temperatures accelerate some of the secondary reactions primarily initiated by UV radiation, so that they proceed faster than, for example, at low or room temperatures. Thus, the extent of the changes in the irradiated polymers is also dependent on the type of thermal analysis used.

However, regardless of the results of the thermal analyses, it can be concluded that the sheets weathered at both exposure sites only exhibited a minimal degree of deterioration and were found to be in a relatively good state. This is not due to any weakness in the outdoor exposure conditions, but it is evidence that the UV stabilization system, based on HALS, performed effectively, providing protection to the polymer at both exposure sites. Good stability and minimal differences between the JGM and Brno samples is promising and there are suitable prerequisites for this product to have a long-service life in outdoor applications.

Conclusions

Changes in the properties of plastics as a consequence of exposure to Antarctic climatic conditions stimulated us to broaden the range of scientific activities at the J.G. Mendel station. Before we carried out our first experiments, there was no public information available on the behaviour of polymers under the relatively harsh Antarctica conditions. Extremely low temperatures, as low as -35°C at the JGM station (Láska et al. 2011), are, on one hand, very friendly to polymers in terms of thermo-oxidation, but the high intensity of UV-A, UV-B radiation during the Antarctic summer promotes polymer photo-oxidation on the other. Both of these, combined with strong winds that contain sand and ice have detrimental effects to the plastics.

The experimental results show that even this extreme location can provide interesting scientific data and extend our knowledge of plastics durability. By introducing polymer testing activities to the J.G. Mendel station we have extended the range of outdoor polymer testing which complements the existing portfolio of test locations where plastics may be exposed to the real conditions of use.

In addition to the systematic scientific research, Antarctic exposure also allows testing of the durability of various utility products that are proposed for use in severe low-temperature polar conditions. By introducing the weathering of plastics to the J.G. Mendel Czech Antarctic Station, we further promoted the noble idea, shared by all the states of the world, that this continent should not be utilized for any other purpose beyond scientific research.

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