Chapter 14
Polypropylene Numerical Photoageing Simulation by Dose–Response Functions with Respect to Irradiation and Temperature: ViPQuali Project

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Abstract The aim of the joint project ViPQuali (Virtual Product Qualification) was to describe a component's ageing behaviour in a given environment, by numerical simulation.

Having chosen polypropylene (PP) as the material, which does not show sensitivity to moisture, the relevant weathering parameters of the dose–response functions could be limited to spectral irradiance and temperature.

In artificial irradiation tests, for PP plates of varied stabiliser content, spectral sensitivity as well as temperature dependence of irradiation-caused crack formation was quantified. For that purpose, samples were exposed both to artificial weathering tests at various constant temperatures and to spectrally resolved irradiation. The temperature dependence could be modelled by an Arrhenius fit. For fitting the spectral sensitivity, a plateau function was chosen. Subsequently, the stabiliser content was parameterised and extrapolated.

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The formed dose–response functions were incorporated into a Computational Fluid Dynamics (CFD) software program, simulating the environment of a sample within a Phoenix-exposed IP/DP (Instrument Panel/Door Panel box) box, based on sun position and weather conditions, including radiation interactions. Observed local effects as well as the general ageing advance of PP hats are compared with respect to simulation and experiment.

Resulting from this project, for this most simple example of PP of varied stabiliser content, the time to failure can be estimated for each weathering exposure environment with known time-resolved irradiance and temperature conditions.

Keywords ViPQuali • Service Life Prediction • Weathering • UV • Spectral sensitivity • Temperature • Polypropylene • Dose–response function (DRF) • PP polypropylene • PP/PE copolymer • Photoageing • Photoaging • Spectral irradiance • Irradiance • Arrhenius • Surface climate • Simulation • HALS

Introduction

Prediction of a product's service life, more precisely of its failure, is a long-existing challenge [1]. However, it can never be given universally, but is always dependent on the respective in use or exposure conditions.

The aim of the joint project ViPQuali[1] was to qualify plastic components for use in arbitrary but defined surroundings [2]. The relevant ageing impact parameters are simulated at the components surface, based on environment geometry and weather data. Then, ageing behaviour is computed, on the basis of empiric dose–response functions (DRF). A fundamental requirement for the concept of DRF is the existence of just one failure property, whose progress can be described quantitatively.

For plastic materials, it is well known that usually the most important weathering parameters are UV irradiance and temperature [3]. Generally, UV radiation initiates photodegradation, whereas temperature influences the kinetics of the autoxidation process ([4], p. 849ff).

For photodegradation, the spectral sensitivity generally is limited to the UV range. However, observing colour changes of pigments and also the VIS range of solar radiation may have influences. Besides, VIS and IR mainly act by radiation heating, reflecting irradiance temperature interactions.

Considering moisture, it is hard to quantify it in its incidence (as considering humidity or wetness of surface microclimates), even harder in its prediction (incorporating radiation and temperature interactions) and hardest in its action on materials ageing ([4], p. 852f). Therefore, for the ViPQuali project, materials and scenarios were chosen, for which moisture influence should not play a major role. Thus, only temperature and irradiance have to be considered, in the concept of DRF.

[1] BMBF, fund no. 01RI05203, 2006–2011

DRF as well as Service Life Prediction itself can be related to a specific failure criterion only. For the DRF concept, the failure property progress is to be quantitatively measurable, additionally.[2]

After all, the DRF has to be formulated as time integral of the multiplied, often coupled sensitivity terms.[3] Taking into account only sensitivity to spectral irradiance[4] and temperature, DRF for a specific material can be written as

$$w(t) = \int_0^t F\left(T\left(t'\right)\right) \int_{\lambda_0}^{\lambda e} s_\lambda \cdot E_\lambda\left(t'\right) \cdot d\lambda \cdot dt'$$

with $w(t)$, property change; λ, wavelength; s_λ, spectral sensitivity of the considered property; $E_\lambda(t)$, time-dependent spectral irradiance at the surface; $T(t)$, time-dependent surface temperature; and $F(T(t))$, temperature dependence term.

Separate, decoupled examination on irradiance and temperature is realised by eliminating surface heating by IR and VIS radiation. Hence, temperature dependence is investigated by irradiation at constant temperatures, in a UVA lamp weathering device. Spectral sensitivity is investigated by spectrally dispersed irradiation, at room temperature.

With additional parameter of varied stabiliser content x, universalised DRF ends in

$$w(t,x) = \int_0^t F\left(T\left(t'\right), x\right) \int_{\lambda_0}^{\lambda e} s_\lambda(x) \cdot E_\lambda\left(t'\right) \cdot d\lambda \cdot dt'$$

For the uncoloured PP of different stabilisations, DRF were created and validated by direct weathering in Phoenix, Arizona [6].

Materials

Originally, four basic materials were investigated in this project. A PP homopolymer as well as a PP/PE copolymer was studied in both an uncoloured and a black type.[5]

Additionally, all four basic materials were stabilised with Hostavin N 30 and Hostanox O 10, in different amounts. Oligomeric HALS (hindered amine light stabiliser) N 30 was added in three different quantities (0.02 %, 0.06 %, 0.1 %).

[2] If necessary, also nonlinearities in the damage increase have to be considered (e.g. saturation in colour change).

[3] Furthermore, for bulk properties, oxygen diffusion can be a limiting factor on timescale. Diffusion can be neglected for surface-related properties only.

[4] Possible dependence of spectral sensitivity on temperature [5] is neglected here.

[5] A very low carbon black amount was added to achieve higher solar heating, but not for stabilisation increase, primarily.

Phenolic antioxidant O 10 was varied between 0 % and 0.044 %. Moreover, each stabiliser combination was prepared twice, independently, to minimise systematic errors.

Then, square plates (8 cm × 8 cm × 0.2 cm) were produced by injection moulding. After all, for each of the four basic materials, the sample plates were produced with 12 independent formulations.

From all four basic materials, components of simple geometry were produced by injection moulding. For this, a geometry of cylindrical hats was chosen. Suspecting earlier failures, these hats were higher stabilised (0.22 % N 30, 0.05 % O 10).

However, first artificial weathering tests showed high time-to-failure durations for the black materials. Due to the limited project run time, efforts were focused on the faster degrading uncoloured materials. Results shown here are only from the uncoloured sample sets.

Methods

Artificial Irradiation

To investigate spectral sensitivity, samples were exposed to spectrally dispersed irradiation [6]. Thus, sample position correlates with the irradiation wavelength. By measuring spectral irradiance as well as property change, spatially resolved, spectral sensitivity can be calculated. For uncoloured PP, the failure by crack formation was quantified as crack formation probability $w(t)$ which was correlated to near-surface carbonyl formation.[6]

For examining temperature dependency, samples were exposed to artificial irradiation at different but constant temperatures. For this, a Weiss Umwelttechnik Global UV Test 200 weathering device was equipped with UVA 340 nm lamps (Type 1A lamp according to ISO 4892-3) and run under dry conditions. By consciously excluding VIS and IR, coupling of irradiance and surface temperature was avoided. UV radiant exposure until failure H_{UV} was determined at the respective temperature, varied between 5 and 65 °C. These limits were chosen to cover the temperature range being relevant for outdoor weathering, avoiding later temperature extrapolations.

Outdoor Weathering

Aiming at later validation, hats of all four materials were exposed in an IP/DP box in Phoenix/Arizona; see Fig. 14.1. This exposure site was chosen, as it features high global solar radiation combined with relative dry climate. Besides avoiding

[6] Measured by FTIR/ATR

Fig. 14.1 All four basic materials (stabilised with 0.22 % N 30) had been exposed in an IP/DP box in Phoenix, for varied durations (3–36 months)

complicated moisture impact, this has the advantage of much more reproducible weather conditions. Additionally, here a wide choice of weathering data is collectable. The IP/DP box weathering scenario can be regarded as a simulation of the exposure of the dashboard behind a window screen inside a car, again roughly excluding moisture effects. By systematically replacing the hats, exposure duration was varied between 3 and 36 months. For the whole exposure time (November 2006 to October 2009), weather data had been recorded.

Numerical Fitting (for Uncoloured PP Only)

As spectral sensitivity curves for different stabilisations did not differ considerably, a common fit was pursued. For this, all data points were equally included. Additionally, an arbitrary data point ($s\lambda$ (1,000 nm) = 0) was added, to enforce the asymptotic behaviour. It can be legitimated by FTIR measurements, after prolonged conditioning and the uncertainty of carbonyl index calculation. To adapt data to the chosen function type, least squares method was used.

For temperature fit, a linear least squares fit of logarithmic radiant exposures and inverse temperatures was used, implying an Arrhenius approach. Separate fits for the respective N 30 content resulted in overlapping activation energies, within their uncertainty ranges. Therefore, a common activation energy was calculated, by including all data points, legitimated by equal temperature positions. Using this common slope, the offsets were determined for the respective N 30 content, separately.

HALS parameterisation was necessary, as the 3D components (hats) were provided with higher HALS stabilisation than the plates for lab investigations.[7] In literature, different approaches can be found. Gugumus studied HALS efficiency [7] and suggested a linear approach for PP, whereas he found square root dependence for PE. However, both assumptions were related to bulk properties, [8] whereas here crack formation as a surface-related property is observed. Therefore, generalising, a power function fit is chosen. With its finite value at zero stabilisation, also an exponential fit could make sense. Thus, the three data points were fitted to a power function, a square root function, and an exponential function as well. Also for these fittings, least squares method was used.

Numerical Simulation of Surface Climate

For numerical simulation, first challenge is computing momentary surface climate of the hats in the IP/DP box, on the base of weather data. Meshing created geometries, attention was paid to sufficient fine structures at borders [8]. For calculating radiation actions, solar radiation had to be divided into direct and diffuse portions. For direct solar radiation, shade formation had to be calculated.

Simulating the surface climate, influence of radiation, convection, and heat flow were investigated, separately, and found that none of them can be neglected [8].

Due to calculational limitations, irradiance was not included and spectrally resolved. Instead, outside the IP/DP box, it was approximated by ASTM G 173-3 spectral irradiance. For glass transmission, angle-independent spectral transmittance was supposed, for the whole range of direct radiation incident.

Taking account of shade formation, radiation interactions, and fluid dynamics, surface climate could be modelled, based on sun position, air temperature, air velocity, and (long wave) environmental radiation data [8].

Numerical Simulation of Ageing Process

Imbedding DRF into calculated irradiance and temperature distribution chronology would give crack formation probability after examined exposure duration.

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[7] Hats were higher stabilised, as otherwise too early failure was expected, in IP/DP box weathering.

[8] For PP, he investigated duration until a specific carbonyl absorbance was found. For PE, 50 % residual tensile strength was examined.

However, very soon it became apparent that simulating continuous sequence of surface climate is not possible, due to computational capability limitations. Instead, azimuth and altitude of sun position as well as corresponding global irradiance were considered in their frequency of occurrence. Also clouding was incorporated, on a statistic basis. For only a few relevant scenarios, full surface climate simulation was computed. Using respective histograms and a linear interpolation approach, ageing progress could be accumulated, for the examined exposure duration [8].

Results

Spectral Sensitivity

Exposure results of spectrally dispersed irradiation are shown in Fig.14.2, for uncoloured PP, and in Fig. 14.3, for the uncoloured copolymer.

For uncoloured PP, the spectral sensitivity could be described as one fit, independent of the stabilisers content [6]; see Fig. 14.2. Thus, for uncoloured PP, DRF can be written as

$$w(t,x) = \int_0^t F\left(T\left(t'\right),x\right)\int_{\lambda_0}^{\lambda e} s_\lambda \cdot E_\lambda\left(t'\right)\cdot d\lambda \cdot dt' = \int_0^t F\left(T\left(t'\right),x\right) \int_{\lambda_0}^{\lambda e} \frac{a_1}{1+\exp\left(\frac{\lambda - a_2}{a_3}\right)} \cdot E_\lambda\left(t'\right)\cdot d\lambda \cdot dt'$$

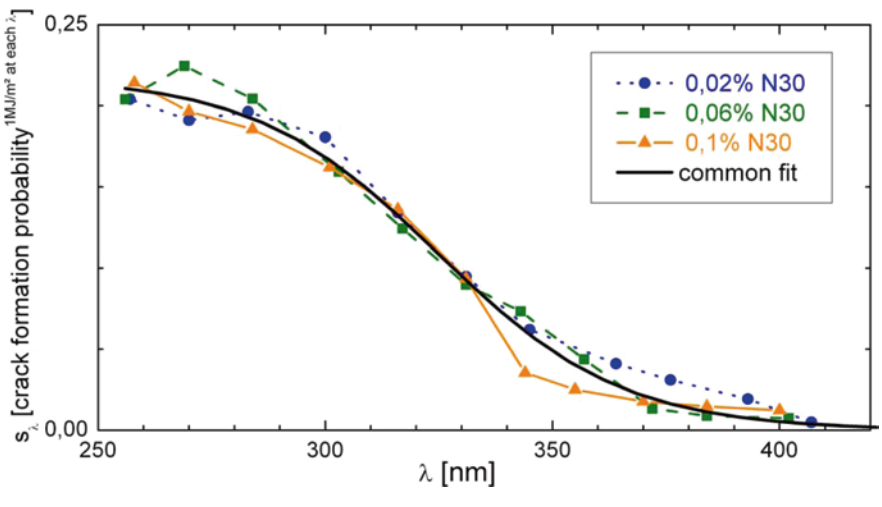

Fig. 14.2 Spectral sensitivity *s*λ fit for differently stabilised uncoloured PP

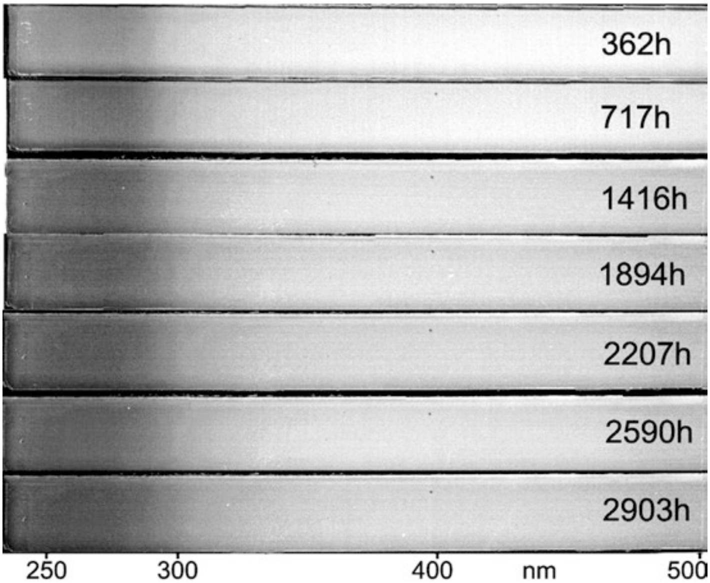

Fig. 14.3 Yellowing (*greyscaled*) after spectrally resolved irradiation, for a PP/PE copolymer of lowest HALS stabilisation

with $a_1 = 0.218 \pm 0.006$ (plateau level), $a_2 = 324.8 \pm 1.9$ (edge), and $a_3 = 20.3 \pm 1.4$ (slope).

For PP/PE copolymer, yellowing was found but limited to the spectral range below 300 nm; see Fig. 14.3. Other changes were not observed, even after about 3,000 h.

Temperature Dependence

For uncoloured PP, temperature dependence of crack formation could be fitted to Arrhenius plots[9]; see Fig. 14.4. Phenolic antioxidant O 10 did not have any effect. Samples failed according to their HALS content and could be fitted to a common (HALS-independent) activation energy. For uncoloured PP, DRF can be changed to

$$w(t,x) = \int_0^t c(x) \cdot \exp\left(\frac{-E_A / R}{T(t')}\right) \cdot \int_{\lambda_0}^{\lambda e} \frac{a_1}{1 + \exp\left(\frac{\lambda - a_2}{a_3}\right)} \cdot E_\lambda(t') \cdot d\lambda \cdot dt'$$

[9] At 5 °C, no failures occurred after 380 MJ/m^2 UV radiant exposure.

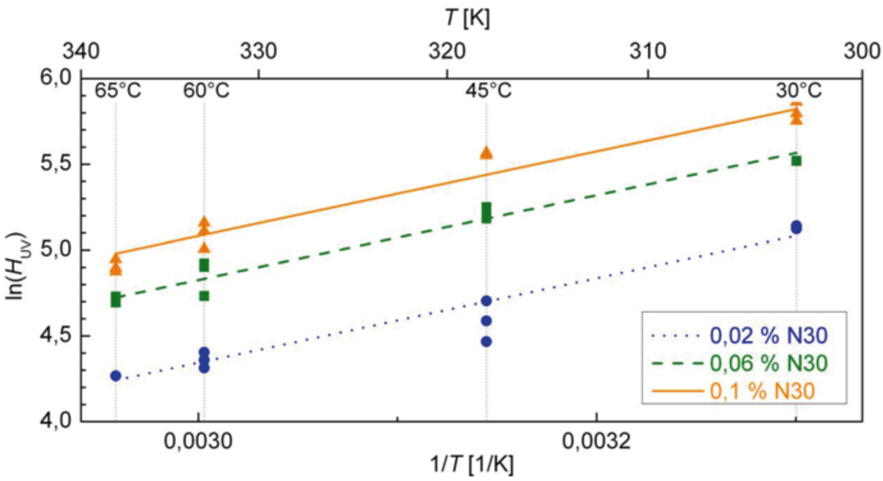

Fig. 14.4 Temperature dependence for differently stabilised uncoloured PP

with $E_A/R = (2{,}464 \pm 344)$ K (resulting in an activation energy E_A of about 20 kJ/mol) and the only stabiliser-dependent parameter $c(x)$.

After weathering device exposure, also PP/PE copolymer failed by crack formation. Yellowing was not observed. Also for PP/PE copolymer, Hostanox O 10 did not have any effect. However, temperature-dependent failure did not follow Arrhenius dependence; see Fig. 14.5.

Parameterisation of the HALS Influence

The fitting results (uncoloured PP) are shown in Fig. 14.6. Using the power function approach, the parameter $c(x)$ was fitted to $c(x) = c_1 \cdot x^{-c_2}$ with $c_1 = 957 \pm 40$ and $c_2 = 0.451 \pm 0.012$.

Dose–Response Function

For the uncoloured PP/PE copolymer, different property changes were observed. After spectrally resolved irradiation at room temperature, it showed yellowing. After irradiation at higher temperatures in a weathering device, it showed micro-crack formation. With those different failure properties, both in the relevant temperature range, DRF could not be completed.

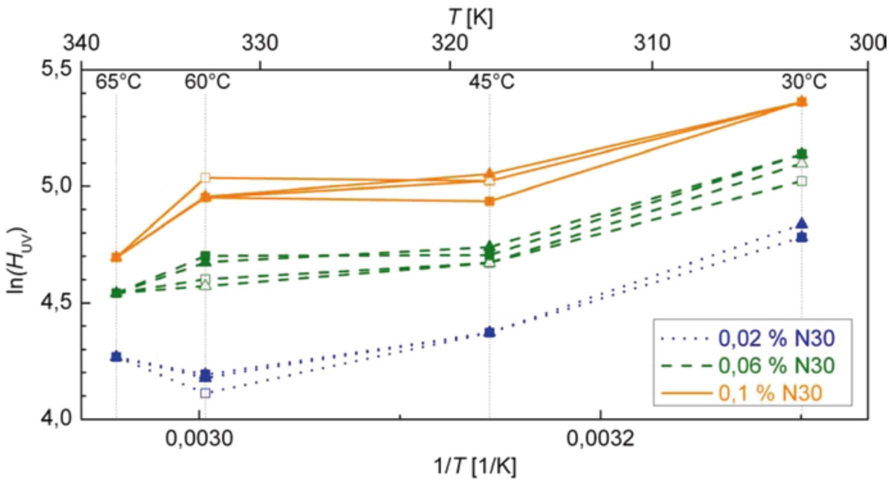

Fig. 14.5 Temperature dependence for differently stabilised uncoloured PP/PE

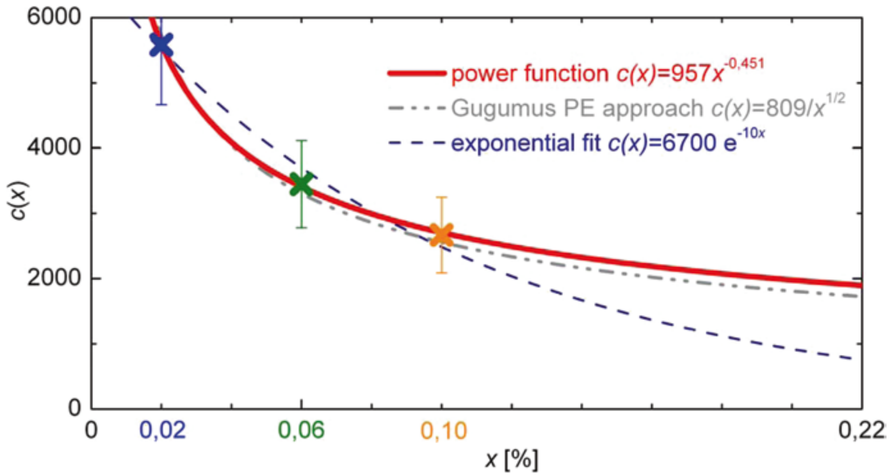

Fig. 14.6 HALS parameterisation for the uncoloured PP, for different fit approaches (three data points and extrapolation point at $x = 0.22$)

Only for uncoloured PP the DRF concept succeeded. With HALS-independent activation energy and spectral sensitivity, Arrhenius temperature dependence, and even stabiliser parameterisation, DRF can be written as

$$w(t,x) = c_1 \cdot x^{-c_2} \int_0^t \exp\left(\frac{-E_A / R}{T(t')}\right) \cdot \int_{\lambda_0}^{\lambda e} \frac{a_1}{1+\exp\left(\frac{\lambda - a_2}{a_3}\right)} \cdot E_\lambda(t') \cdot d\lambda \cdot dt'$$

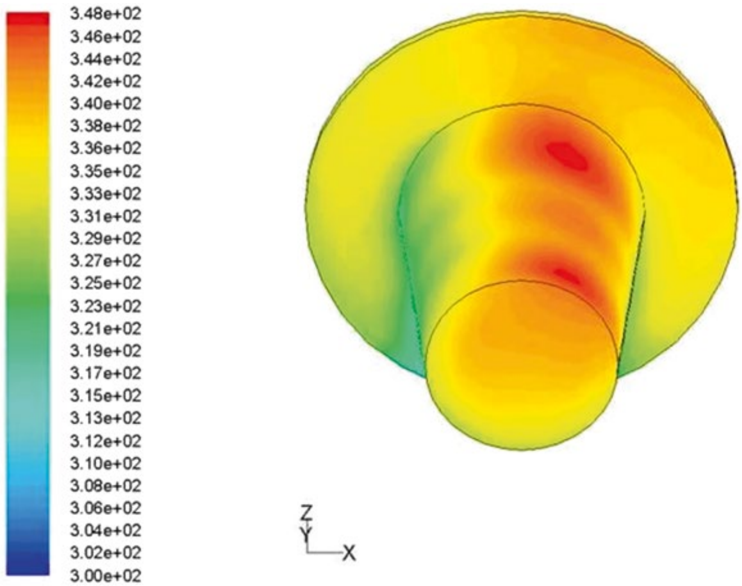

Fig. 14.7 Calculated surface temperature distribution for Phoenix, 24th June, high noon

with $c_1 = 957 \pm 40$, $c_2 = 0.451 \pm 0.012$, $E_A/R = (2{,}464 \pm 344)$ K, and $a_1 = 0.218 \pm 0.006$, $a_2 = 324.8 \pm 1.9$, and $a_3 = 20.3 \pm 1.4$.

Numerical Simulation of Surface Climate

Surface irradiance and temperature distribution were computed, on the base of weather data. Figure 14.7 shows computed surface temperature distribution, for 24th June, high noon. Circular shapes result from local fluid flow effects [8].

Numerical Simulation of Ageing Process

Knowing frequencies of all irradiance and surface temperature distributions over the specific period, the ageing evolutions can be accumulated, using DRF of uncoloured PP. Figure 14.8 shows calculated damage distribution, after 31 months' IP/DP box exposure. Crack formation occurs at values higher than 1.

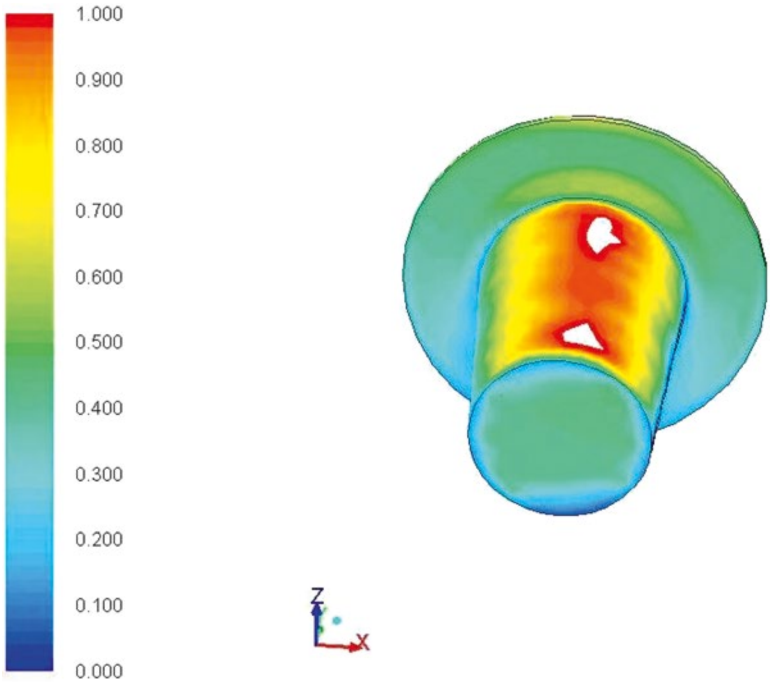

Fig. 14.8 Calculated failure probability distribution after 31 months IP/DP box irradiation

IP/DP Box Exposure Results

After IP/DP box exposure, hats were visually inspected. After 2 years, no damage was noticeable. Only the uncoloured PP hat exposed for 36 months showed intensive surface crack formation, as ring-shaped damages; see Fig. 14.9.

Discussion

Breaking down in Service Life Prediction of the uncoloured PP/PE copolymer proves the necessity of a clear failure property or a single, dominant degradation process, respectively. Geuskens [9] mentioned different effects at different wavelength irradiances. According to [10], at least hydroperoxide decomposition may proceed thermally or photochemically. However, method of spectrally dispersed irradiation is suited only for primary reactions of degradation process [11].

In contrast to uncoloured PP/PE, the missing success with both black-coloured materials is mainly owed to the limited project run time and the too high failure durations.

However, for one of the four investigated materials, a conclusive DRF was created. For spectral sensitivity, the plateau function fit, with its limited sensitivity

Fig. 14.9 Surface crack formation after 36 months IP/DP box exposure (view inside the PP hat from bottom to top)

towards smaller wavelengths, is not allowed to be extrapolated below 250 nm. Here, an explicit increase is expected, but could not be proved within the used measuring range.

For determining temperature dependency, the chosen range for laboratory tests should avoid later temperature extrapolations, which are often a source of errors. Cancelling the 5 °C irradiation after 380 MJ/m^2, this only partially succeeded. For comparison only, according to an Arrhenius fit, failure should have occurred at 5 °C, after 330, 530, and 690 MJ/m^2, respectively, with uncertainties of about 100 MJ/m^2. However, with maximum black hat surface temperature of about 75 °C (Fig. 14.7)[10] and most frequently values between 31 and 73 °C [8], the considered test range made sense.

In the end, stabiliser parameterisation was indispensable for succeeding in this project. However, it was not foreseeable that one stabiliser would show no action, at all, and that the other's action could be described independent on temperature and wavelength. Afterwards, it can be stated that phenolic antioxidant O 10 as a thermal stabiliser probably acts at higher temperatures and that activation energy does not depend on the HALS N 30 content.

However, in regard to both damage distribution and damage progress, simulation and exposure results of the uncoloured PP show good accordance.

The computed surface climate is consistent with measured surface temperatures (black standard temperature) at different IP/DP box walls [8]. Components surface

[10] Maximum surface temperature for uncoloured PP is about 10 K lower.

temperature distribution is strongly influenced by convective fluid flow. The observed ring-like damages result from local fluid flow effects, but not from component production problems.

For the ageing progress estimation, some approximation had to be done. A statistic approach of sun position and corresponding global irradiance was necessary, due to capability limitations. Also clouding was incorporated, on a statistic basis. Both simplifications do not relevantly influence the ageing results.

Huge uncertainties result from extrapolation of HALS parameterisation.[11] As can be seen in Fig. 14.6, all approaches would fit within uncertainty limits. However, at hat stabilisation of $x = 0.22$, the exponential fit would result in a much slower ageing (factor 2.5). The power function fit was chosen for the DRF, as it reflects current state of the art. But with its finite value at zero stabilisation, also an exponential fit could make sense. However, this demonstrates the large uncertainties of an extrapolation, over such a huge range. Depending on the respective approach, predicted ageing could be doubled.

Whereas this strategy conditioned factor 2 complicates a quantitative evaluation, damage distribution shows very impressive accordance.

Conclusions

For differently stabilised, uncoloured PP, the weathering sensitivities were quantified. Spectral sensitivity was fitted to a plateau function. Temperature dependence was described as an Arrhenius fit. The action of HALS stabiliser content (Hostavin N 30) was parameterised by a power function fit, whereas the phenolic antioxidant Hostanox O 10 did not show any influence on the ageing behaviour.

The relevant input data (irradiance and temperature direct at the surface) were calculated for a 3D component, on the basis of weather data, including shade formation, radiation interactions, and fluid dynamics.

Incorporating dose–response functions, the 3D ageing behaviour was computed, for IP/DP box exposure in Phoenix, Arizona.

The computed ageing behaviour correlated very well with both ageing processing and damage distribution.

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[11] This could be clarified by further experiments only (e.g. IP/DP box exposure of lower stabilised PP hats). However, ViPQuali project finalised.

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