Hot air aging behavior of polypropylene random copolymers

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ABSTRACT: This article deals with the global aging behavior of three polypropylene random copolymer (PP-R) materials with varying primary structure and morphology. Hot air aging experiments at elevated temperatures from 95 to 135 °C were carried out using micro-sized specimens with a thickness of 100 μm. Technological and analytical aging indicators were monitored for an exposure time of up to 750 days. Independent of comonomer type (ethylene vs. butylene) and morphology (α vs. β crystal form) a critical molar mass of 300 kg mol⁻¹ was obtained. The consumption of antioxidants was slower for the β-nucleated PP-R grade with finer spherulitic structure. The β-grade outperformed the α-crystal PP-R grades resulting in about 20% higher time-to-embrittlement values. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2019, 136, 47350.

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INTRODUCTION

To tailor the properties of polypropylene (PP), the morphology is commonly adjusted by the copolymerization with α-olefin comonomers or by the addition of nucleating agents. For example, random copolymers with <5 wt % of ethylene are used in hot water applications. With increasing comonomer content, the copolymer exhibits smaller crystallites and enhanced tie molecule density resulting in improved impact toughness and long-term creep resistance. Also nucleating agents are used to modify the crystalline structure and to improve the temperature resistance. Better toughness and creep properties are reported for β-nucleated PP-R grades compared to non-nucleated grades with α-crystal structure.

The long-term thermo-oxidative behavior of polymeric materials is commonly investigated by oven aging tests at elevated temperatures. Hot air aging experiments of PP copolymers with different comonomer or nucleation are quite scarce. Gugumus investigated the hot air aging behavior of PP homopolymers extensively. A significant effect of the different stabilizer systems was deduced. Preliminary investigations on the hot air aging behavior of PP block and random copolymers have been carried out by Povacz et al. or Grabmayer et al. At an exposure temperature of 135 °C, a significant effect of the pigment type (carbon black vs. carbon nanotube), the stabilizer system, and also the specimen thickness has been reported in the previous work. So far, no comprehensive studies on the effect of both, comonomer type and nucleating agent on the long-term aging behavior of polypropylene random (PP-R) copolymers were published. Hence, it is the main objective of this article to evaluate the effect of ethylene or butylene comonomers and α- or β-spherulitic structure on the aging behavior of PP-R copolymers.

The investigated materials of this work are typically used in hot water applications. The long-term stability of PP-R copolymers against thermo-oxidation and the ductile material behavior is essential to ensure functionality and durability at service temperatures up to 95 °C. These outstanding material properties of PP-R resulted in an increased amount of use for solar thermal systems. Depending on the application, PP-R is used as a thin, black-pigmented absorber material for solar thermal heating as well as up to 3 mm thick liner material for seasonal heat storage systems.

METHODOLOGICAL APPROACH

Materials, Specimens, and Aging Conditions

Three commercial PP-R grades designated PP-REα, PP-RBα, and PP-REβ suitable for hot water applications were selected for the investigations. The indices E (ethylene) and B (butylene) designate the comonomer of the random copolymer. The indices α and β represent the crystal structure (α: monoclinic, β: hexagonal). To investigate the effect of comonomer and morphology, the materials exhibited similar stabilizer systems based on the
phenolic antioxidants Irganox 1010 and Irganox 1330. The overall amount of phenolic antioxidants was higher for PP-RBα and PP-Rββ and lower for PP-Rγε. The Irganox 1010 to Irganox 1330 ratio was 1.0 for PP-Rεε, 0.3 for PP-RBα, and 0.4 for PP-Rββ. All grades exhibited on specimen level < 0.1 wt % of Irgafos 168 processing stabilizer. The amounts of stabilizers were attributed to the base-stabilization package of the commercial grades selected by the polymer manufacturer. No additional stabilization was used in this work.

AGRU Kunststofftechnik GmbH extruded 2 mm thick sheets on an Extrudex EN 45-25D extruder. For aging experiments 100 μm thick micro-sized specimens were prepared by automated, computerized-numerical-control-aided edgewise planning. Hot air exposure was performed at 95, 105, 115, 125, and 135 °C in Binder FED 53 (Tuttlingen, Germany) heating chambers with forced circulation. These temperatures were selected to point out the temperature dependent aging effects. Comparable exposure conditions for aging experiments of PP were used and published by different researcher. At defined time intervals, four specimens were removed and characterized.

Aging Characterization
Aging characterization was performed using analytical and technological methods. To monitor especially stabilizer-related changes in the induction period, high-pressure liquid chromatography coupled with ultraviolet spectrometry (HPLC-UV), infrared (IR) spectroscopy, and differential scanning calorimetry (DSC) were used. Furthermore, material changes and ultimate failure characteristics were characterized by gel permeation chromatography (GPC), IR spectroscopy and tensile testing.

To examine the stabilizer consumption a validated HPLC approach using a water/acetonitrile mobile phase gradient was applied. A measurement uncertainty of about 8% is given for the used HPLC device (1260 Infinity, Agilent Technologies, Santa Clara, CA) with a Kinetex C18 separation column (50 × 3 mm, 2.6 μm particle size) coupled to an UV-detector at 200 nm. To compensate stabilizer losses and avoid stabilizer degradation reactions during sample preparation, Irganox L109 was added as internal standard and tributylphosphite as oxidation protection. The detection deviation limit of the system is 0.003 wt %. The drop below 0.01 wt % was defined as critical limit value. After oxidation of a single phenolic functionality, the phenolic antioxidant molecule cannot be quantified anymore by HPLC despite, there is still a remaining stabilizing effect. The content of nonoxidized phenolic antioxidants was evaluated quantitatively as aging indicator, as no standards are available for their (partially) oxidized forms.

IR spectroscopy (Perkin Elmer Spectrum 100, Waltham, MA) in transmission mode was used to derive the phenol index, which was correlated with the quantitative HPLC data. The integral of the peak centered around 3646 cm⁻¹ (phenol related peak) was normalized by the integral of the neighboring peak of 3765 cm⁻¹, which can be attributed to the aging-affected aluminum oxide groups of the co-catalyst. The IR method allows characterizing also the partially oxidized forms of phenolic antioxidants.

Thermal analysis was performed on a DSC 4000 (Perkin Elmer). Samples of about 3 mg were taken from the cross section of the micro-sized specimens. Samples were heated up to 300 °C in perforated 3 μL aluminum pans at a heating rate of 10 K min⁻¹. As purge gas air was chosen with a constant gas flow of 20 mL min⁻¹. The dynamic oxidation onset temperature was evaluated by the intersection of the extended baseline with the extrapolated slope of the exotherm.

Molar mass (Mw) of the investigated PP-R grades was examined by high temperature gel permeation chromatography (HTGPC) system from PolymerChar (Valencia, ESP) equipped with an IR 5 detector. The separation was performed using 3 PLgel Olexis columns (300 × 7.5 mm) with 1,2,4-trichlorobenzene (TCB) at 160 °C as mobile phase. A sample mass of 2 mg was dissolved in 8 mL TCB. In addition, heptane was added as a flow marker to compensate shifts in the retention volume. A calibration was done using PP standards.

IR spectroscopy was also performed to examine the molecular changes of the polymers. Therefore, the specimens were measured in attenuated total reflection (ATR) mode. The carbonyl index was derived from the ratio of the CO-stretching peak at 1715 cm⁻¹ and the CC-stretching peak at 974 cm⁻¹.

Ultimate mechanical properties were characterized by tensile testing of the 2 mm broad and 100 μm thick micro-sized specimens on a screw-driven universal testing machine (Zwick Line Z2.5, Ulm, Germany). In accordance with ISO standard, 527 tests were performed at ambient temperature with a gauge length of 50 mm and a test speed of 50 mm min⁻¹. Strain-at-break values were monitored over the aging period. As limit value ultimate failure was classified when strain-at-break values dropped below the strain-at-yield value (εb < εy). For the investigated grades, the strain-at-yield was 17%. As pointed out by Maier et al., the yield point of semicrystalline polymers with spherulitic structure is characterized by the initiation of interspherulitic cavitation. If strain-at-break is below strain-at-yield, the interspherulitic tie molecule density is too low to induce further plastic deformation mechanisms such as spherulitic breakdown and fibrillation.

RESULTS AND DISCUSSION
Temperature/Time Dependent Antioxidants Deterioration
In Figure 1, the aging-induced deterioration of phenolic antioxidants of the PP-R grades is illustrated for different exposure temperatures. To compare the materials, the total concentration of nonoxidized phenolic antioxidants was used as aging indicator. The phenolic antioxidant concentration (Irganox 1010 + Irganox 1330) of the unaged samples was 0.40 wt % for PP-Rεε and 0.55 wt % for PP-RBα and PP-Rββ. The ratio between Irganox 1010 and Irganox 1330 was 1.0, 0.3, and 0.4 for PP-Rεε, PP-RBα, and PP-Rββ, respectively. Hot air aging led to an exponential decay of nonoxidized phenolic antioxidants. Although, PP-Rεε exhibited a lower concentration of antioxidants in the reference state, the amount of nonoxidized antioxidants aligned in the induction period. This alignment phenomenon was faster at higher exposure temperatures. Interestingly, for all PP-R grades, the total deterioration of nonoxidized antioxidants was obtained at the same aging time independent on the comonomer type and...
morphological structure well before the end of the induction period characterized by full embrittlement. As pointed out by Maringer et al. for PP, polymer additives are preferentially located at the interface of spherulites. In PP-R copolymer films, the crystallization rate is reduced leading to imperfect spherulites characterized by an asymmetric sheaf-like structure with dimensions in the range between 1 and 5 μm. The dimensions of such sheaf-like structures are smaller at higher comonomer content. For none of the investigated grades, spherulites were discernible by polarized optical microscopy. Therefore, PP-RE β should exhibit a more homogenous distribution of antioxidants due to a finer spherulite structure with spherulite diameters below 10 μm. The alignment phenomenon is presumably related to oversaturation of phenolic antioxidants. Slightly higher amounts of nonoxidized phenolic antioxidants were detectable in the induction period for the β-nucleated grade with finer spherulitic structure, especially at the lowest temperature of 95 °C. As described by Beißmann et al. for Irganox 1330, the deterioration of phenolic antioxidants is partially related to oxidation of the phenolic functional group. A further physical effect is the diffusion and evaporation of the antioxidants. The solubility and rate of evaporation in hot air is dependent on the specific formulation of polymeric materials. Although, PP-Rβ and PP-REβ exhibited the same initial antioxidant concentrations, a more pronounced drop of antioxidant content was obtained within the first aging period.

In Figure 2, the time/temperature dependency of the total deterioration of phenolic antioxidants [i.e., concentration of nonoxidized phenol is below the detection limit (AO<0.01 wt %)] is plotted in an Arrhenius diagram. Due to the fact that both, chemical degradation (e.g., oxidation) and physical aging (diffusion) are following Arrhenius relationships an excellent fit with a coefficient of determination of 0.98 was obtained. For time to total deterioration of phenolic antioxidants of the PP-R grades, the linear Arrhenius extrapolation resulted in aging times of about 10 and 50 years at exposure temperatures of 65 and 40 °C, respectively.

To evaluate and quantify also the amount of partly oxidized phenolic antioxidants, the phenol index (PI) was determined by IR spectroscopy in transmission. The PIs are depicted in Figure 3 as a function of time and temperature. The initial PI values of the unaaged samples were about 4.3 for PP-REα and approximately 6.0 for PP-RBα and PP-REβ. The initial phenol indices correlated well with the initial values of nonoxidized phenolic antioxidant content determined by HPLC. Interestingly, the decay of the PI was less pronounced and less exponential but more linear compared to the concentration of nonoxidized phenolic antioxidants.

![Figure 1. Nonoxidized phenolic antioxidant concentration of PP-R specimens as a function of aging time exposed in hot air at 135, 125, 115, 105, and 95 °C.](wileyonlinelibrary.com)

![Figure 2. Time/temperature dependency of the deterioration of phenolic antioxidants for the model PP-R grades.](wileyonlinelibrary.com)
Also the alignment phenomenon was less distinct for the PI values. PI values of about 2.0 were deduced at full deterioration of the nonoxidized phenolic antioxidants. The open symbols represent fully embrittled specimen with strain-at-break values below yield point. Except the data point for PP-RB at an exposure temperature of 135 °C for all samples the end of induction period associated with full embrittlement was obtained at PI values below 1.0.

In Figure 4, the PI values are plotted versus the concentration of nonoxidized phenolic antioxidants. On basis of the used HPLC method, a critical limit of 0.01 wt % was set as limit for consumption of antioxidants. Hot air aging resulted in decreasing antioxidant content and decreasing PI. A linear relationship with a sufficient high coefficient of determination ($R^2 = 0.90$) was obtained for antioxidant contents greater than the detection deviation limit. The intercept of the linear fit and the detection deviation limit gives a critical PI where at least one functional group is oxidized in the stabilizer molecules. A PP-R grade independent critical PI of 2.2 was obtained. Below this limit, the PI is further decreasing with aging time due to further oxidation or loss of already partly oxidized phenolic antioxidant molecules.

The dependency of oxidation temperature of the three PP-R grades on hot air aging at temperatures ranging from 95 to 135 °C is shown in Figure 5. Oxidation temperature serves as an aging indicator to monitor the content of active antioxidants and the degradation of the polymer.\textsuperscript{10,12,28} The initial oxidation temperatures of the unaged samples were in the range from 267 to 271 °C with higher values for PP-RB$\alpha$ and PP-RE$\beta$ exhibiting higher amounts of antioxidants. Within the first aging intervals, an initial drop up to 15 °C of the oxidation temperature was observed for all exposure temperatures. This drop is related primarily to physical loss like evaporation of the antioxidants and was more pronounced for the $\alpha$-crystalline PP-R grades.\textsuperscript{13} A steady decrease in oxidation temperature was monitored for all PP-R grades with faster decline at higher exposure temperatures. Interestingly, similar oxidation temperature values were deduced for the $\alpha$-crystalline PP-R grades although the initial antioxidant content was significantly higher for PP-RB$\alpha$. PP-RE$\beta$ exhibited slightly higher oxidation temperatures (~5 °C) especially at longer aging times. This is in agreement with slightly higher nonoxidized phenolic antioxidant contents or PI values for the $\beta$-grade. The vertical dashed lines indicate the aging times when all phenolic antioxidants were at least partially oxidized. Beyond this limit, the decay of oxidation temperature is slightly more pronounced. Further hot air aging led to ongoing reduction in
oxidation temperatures to critical values of approximately 210 °C associated with full embrittlement of the specimens. Weakly dependent on aging temperature and the specific grade full embrittlement was obtained at oxidation temperature values ranging from 200 to 212 °C. Although for PP-REβ, the critical oxidation temperature value of about 200 °C was independent on aging temperature, the critical oxidation temperature values were decreasing from 212 to 200 °C for the α-grades PP-REα and PP-Rβα with reduced temperatures from 135 to 115 °C. Hence, the oxidation temperature does not unambiguously reflect the end of the induction time for investigated grades and temperatures. As shown by Grabmayer et al. the critical oxidation temperature is also dependent on the stabilizer system but almost independent on the specimen thickness. Presumably, the lower critical oxidation temperature values of the PP-REβ grade are related to additional stabilizers such as small amounts of thiosynergists (e.g., Irganox PS-800 or 802 by BASF (Ludwigshafen am Rhein, Germany)).

**Polymer Degradation and Embrittlement**

Figure 5 depicts the average molar mass values of the random copolymers as a function of hot air aging time and temperature.

![Figure 5. Oxidation temperature values of PP-R specimens as a function of hot air aging time and temperature.](image1)

Figure 6 depicts the average molar mass values of the random copolymers as a function of hot air aging time and temperature.

![Figure 6. Molar mass of PP-R specimens as a function of aging time and exposure temperature.](image2)
Although the PP-R grades are based on different comonomers and nucleating agents, the molar mass reference values are in the same range of 775 kg mol$^{-1}$. These values are in good agreement with data provided by Kahlen et al.\cite{18} for PP-R copolymers. Interestingly, hot air aging at all investigated temperatures resulted in an initial decrease of about 5% within the first 500 h for all PP-R grades. Hence, both chemical and physical aging processes occurred already in the induction period. Hot air aging resulted in a steady decrease of molar mass until ultimate failure (indicated by open symbols in Figure 6) with higher gradients at higher exposure temperatures. The observed decay in average molar mass is in contradiction to the well-established concept of induction period with negligible chemical changes of the macromolecular structure. The results clearly indicate that local aging phenomena take place in the materials related to limited homogeneity of the stabilizer distribution, the heterogeneous, semicrystalline morphology of the investigated PP-R copolymers and diffusion processes of oxygen and stabilizers. As shown by Grabmayer et al.\cite{13}, the embrittlement times for PP specimens are dependent on the thickness also confirming the concept of diffusion limited oxidation (DLO) postulated by Celina.\cite{16} Ultimate failure of the specimen was obtained at a critical molar mass value of 300 kg mol$^{-1}$ almost independent on temperature (for 135, 125, and 115 °C) and the specific grade. This critical molar mass value is higher compared to data of 150–230 kg mol$^{-1}$ published by Fayolle et al.\cite{29,30} for isotactic PP homopolymers. Fayolle et al.\cite{30} also pointed out that the critical molar mass values are independent on exposure temperature and probably only slightly influenced by the morphological structure as long as the degree of crystallinity is in the same range. The melting enthalpy of the investigated PP-R grades was in a comparable range of about 60 J g$^{-1}$. Hence, the independency of the critical molar mass of 300 kg mol$^{-1}$ for the investigated PP-R grades with different comonomers and crystalline structure is corroborating the findings of Fayolle et al.\cite{30} for PP homopolymers. At 105 and 95 °C, so far no full embrittlement has been achieved. The maximum exposure times are 10 000 h for 105 °C and 15 000 h for 95 °C. These experiments are still ongoing and will be continued.

The carbonyl index (CI) values are depicted in Figure 7 as function of aging time in hot air at 135, 125, 115, 105, and 95 °C. The initial CI values of the investigated PP-R grades were about 0.1. As a result of hot air aging, the CI of the specimen surface slightly raised to values of about 0.2–0.4. Interestingly, a higher attained CI plateau was obtained for lower exposure temperatures. As indicated by the open symbols, the CI values increased significantly to values of more than 0.5 for the fully embrittled specimen. At exposure temperatures of 105 and 95 °C, no embrittlement was achieved so far. The aging-induced CI changes were also not significantly affected by the polymer morphology or the comonomer type.

Finally, the strain-at-break values of the investigated PP-R grades are illustrated in Figure 8. Ultimate failure with strain-at-break values below yield point is indicated with open symbols in the chart. The unaged 100 μm specimens revealed highly ductile behavior with strain-at-break values of 550−700%. Within first 500 h of hot air exposure, the β-nucleated grade PP-REβ exhibited a significant drop of strain-at-break with remaining values around 50% for the aging temperatures from 95 to 125 °C. This drop is presumably related to postcrystallization effects and more pronounced internal stress between the sheaf-like structures.\cite{4,24–26} A less pronounced initial decrease was obtained for PP-REβ at 135 °C. However, DSC experiments clearly indicated a β-to-α-transition at this aging temperature, which is already in the maximum of the β-crystal melting peak of 133 °C. The investigated PP-REα revealed nonconsistent trends with a pronounced initial drop at 135, 115, and 95 °C, but almost no reduction at 125 and 95 °C. This inconsistency is presumably attributable to the fixation of the specimen in the sample holder.

**Figure 7.** Carbonyl index of PP-R specimens as a function of aging time exposed in hot air at 135, 125, 115, 105, and 95 °C. [Color figure can be viewed at wileyonlinelibrary.com]
The applied stress was not controlled and presumably differing. The grade PP-RBα exhibited almost no initial changes of strain-at-break values (εb > 500%). The highest exposure temperature of 135 °C is located quite close to the area of melting temperature of the PP-R materials resulting in higher mobility of molecular chains and melting of smaller spherulitic structures. In addition, for all investigated materials, the recrystallization temperatures are in the range of 95 and 115 °C. As described by Wang et al.31 and Mollova et al.,32 polymer morphology changes because of chain mobility and isothermal crystallization are strongly temperature dependent.

For all PP-R grades, ultimate failure occurred in hot air at 135, 125, and 115 °C within 16 000 h. Ultimate failure first appeared at 135 °C after 1750 h for PP-RBα. Due to the used butylene comonomers in PP-RBα, the melting temperature is reduced to about 137 °C. Thus, the exposure temperature was only a few degrees lower than the melting temperature and the fraction of crystallinity was lowest for this grade at 135 °C. The embrittlement times of the PP-REα and PP-REβ grades were 3300 h. The aging behavior due to different morphology was unincisive presumably related to the β-to-α-transition for the PP-REβ grade at 135 °C. Although the embrittlement times of 5970 and 13 340 h at 125 and 115 °C, respectively, were comparable for the grades PP-REα and PP-RBα, the β-nucleated grade revealed about 10% higher embrittlement times of 6800 h at 125 °C and 14 370 h at 115 °C. The failure times clearly indicate that the type of comonomer does not affect the hot air aging performance. The slight positive effect of the β-crystal form is presumably related to sheaf-like structure with enhanced interspherulitic entanglements.16,33 As shown by Grabmayer et al.,13 additional stabilization of β-nucleated PP-R grades with stabilizer packages containing thio-synergists or aromatic amines will result in about 20% higher long-term aging endurance times in 135 °C hot air.

**SUMMARY AND CONCLUSION**

To assess the effect of ethylene and butylene comonomers and α- or β-spherulitic structure on the global aging behavior, three commercial PP-R copolymers were exposed hot air at temperatures ranging from 95 to 135 °C for up to 750 days. Analytical and technological tests were carried out on 100 µm thick specimens to evaluate differences in long-term thermal aging behavior. Temperature/time dependent antioxidant deterioration and the global polymer degradation were investigated extensively.

For all PP-R grades, an exponential decay of nonoxidized antioxidants was detected determined by HPLC. The amount of nonoxidized antioxidants aligned over the aging periods resulting in equal times of total consumption. Hence, an oversaturation of phenolic antioxidants was assumed. The deterioration of antioxidants followed an excellent Arrhenius relationship resulting in total phenolic antioxidant consumption after 10 years at 65 °C. By evaluating the PI, also partially oxidized phenolic antioxidants with remaining stabilization effect were considered resulting in a linear decrease of PI over the aging time. A critical PI of 2.2 was obtained where at least one functional group is oxidized in the stabilizer molecules. The oxidation temperature also serves as an aging indicator for the consumption of antioxidants. During the aging experiment up to 5 °C higher oxidation temperatures were monitored for the β-nucleated PP-R grade. A weakly temperature and material dependent critical oxidation temperature for embrittled specimens ranging from 212 to 200 °C was obtained.

The strain-at-break values of the investigated PP-R grades were dropping after hot air exposure within the first 500 h. This initial drop was attributed to physical aging mechanisms and was less pronounced for PP-RBα. Interestingly, an initial decrease in about 5% in molar mass indicated a superimposition of chemical
and physical aging mechanisms during induction period. An improved aging behavior was obtained for the β-spherulitic PP grade (PP-REβ) with about 10% higher ultimate failure times in 135, 125, and 115 °C hot air, whereas the investigated comonomer types did not affect the hot air aging behavior. Embrittlement of all PP-R grades resulted in sudden increase of the CI as well as a temperature and PP-R grade independent critical molar mass of 300 kg mol⁻¹.

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