

# **POLYPROPYLENE DEGRADATION AND DURABILITY ESTIMATES BASED ON THE MASTER CURVE CONCEPT**

Lecon Woo, Michael Ling, Atul R. Khare, and Y. Samuel Ding  
*Baxter International, Round Lake, IL 60073*

## **INTRODUCTION**

Material degradation and life prediction studies need to overcome numerous challenges. Among the most formidable is the long term real time data generation. The typical experimental time span seldom goes beyond a year, and various ways to accelerate the ageing process frequently encounter fundamental difficulties which reduces the value of the extrapolation or worse, totally negate it.

F. Gugumus (1989) examined the oven stability of a polypropylene film for up to about 1.5 years between 40 and about 105°C, and the apparent activation energy in the Arrhenius plot was clearly variable with respect to temperature with a diminishing trend toward lower temperatures.

Recently, when we examined a large amount of data over broad temperature ranges, including our own, for a variety of polymers, we also noted the general increasing trend of the apparent activation energy temperature. This changing activation energy, or curvature in the Arrhenius plot, could be the major source of error in extrapolating from high temperature, short term data to near ambient long term life-time predictions.

With this background, we began the search for experimentally demonstrable generalizations in selected polymer systems to guide further study.

## **EXPERIMENTAL**

A very stable (including manufacturing process, catalyst system and antioxidant package for over 20 years) medical grade polypropylene random copolymer (PP1) with about 2 wt.% ethylene content and melt flow of about 1.5 dg/min and stabilized with (2,4,6-tris-(3',5'-di-t-butyl-4'-hydroxybenzyl)1,3,5-trimethyl benzene ) and with about 100 ppm of calcium stearate as the acid scavenger was chosen as the primary system for study. A second sample, a radiation grade (totally different process and producer) random copolymer (PP2) with about 2.5wt.% ethylene and 25 melt flow and stabilized only with a hindered amine light stabilizer (HALS) with a phosphite synergist was also used in this study. In addition, a black pigmented, highly stabilized construction grade homopolymer (PP3) with unknown antioxidant package was used for comparison. In addition, limited data were taken from a oriented polypropylene film (OPP) with unknown antioxidants.

Technique used in this study includes ASTM D3895-92 isothermal oxidative induction time (OIT) using a Dupont 1090 thermal analyzer with 910 differential scanning calorimetry (DSC) cell. Contrast to ASTM method which specifies a fixed

temperature, we adopted a method similar to N. Billingham et al (1981) to cover a wide temperature range. High oxygen pressure OIT was conducted with a TA Instruments high pressure DSC cell. Scanning Electron Microscopy (SEM) morphological analysis was conducted with a JEOL 6300 FESEM or a JEOL 35CF instrument after sputter coating with palladium for surface conductivity. Gamma exposure at various doses was conducted in a gamma cell at a dose rate of approximately 6 kGy/hr. A more recent irradiation experiment was carried out with an electron beam irradiator with 10 MeV energy at significantly higher dose rates. Typically, film samples between 150 and 250 microns in thickness were used unless specified otherwise. Digitally controlled forced convection air circulating ovens were used at various temperatures to assess long term oven stability with sample embrittlement as end points.

## **RESULTS AND DISCUSSION**

Catastrophic failures have been reported during the PP post irradiation shelf life storage period. Intense investigation has come to the following working model, that long lived free radicals trapped in the crystalline domains slowly migrate towards the crystalline /amorphous interface where they react with available oxygen to form peroxy and hydroperoxy radicals and initiate degradation near the interface as reported by Rolando (1993) and Woo et al.(1996) among others. When sufficient number of the tie molecules between crystallites were cut through this chain scission process, PP's elongation is reduced dramatically and catastrophic failures followed.

Since antioxidants in PP reside primarily in the amorphous phase, its effectiveness to react preferentially with primary free radicals governs the overall post irradiation stability. In an earlier study, PP2's OIT under air flow conditions of 100 ml/ min was determined and the result compared with the same film sample (about 130 micron in thickness) after 20 kGy of gamma dose. When the data was plotted in the Arrhenius form in Figure 1, it is clearly seen that the gamma exposure has significantly reduced the OIT over the entire temperature range. In addition, the reduction factor appeared to be relatively constant, and the resulting approximately parallel curves hinted that a "self-similarity" may exist for this sample. To access still lower temperatures, where the OIT detection becomes difficult, the gamma-exposed films were subjected to oven aging at 90 and 60°C and their failure times noted. When the oven failure times were plotted onto the Arrhenius plot with the gamma samples, a continuous curve emerged (Figure 2). This continuity observed for PP2 was also seen in other polyolefin systems, namely, at a given temperature, for similar geometry samples, depletion of the antioxidants detected by OIT also marks the onset of embrittlement failures in oven aging.

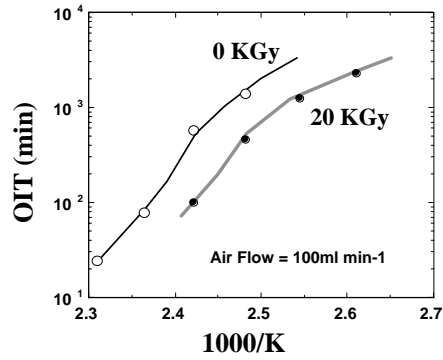


Figure 1. PP2 OIT at 0 and 20 kGys.

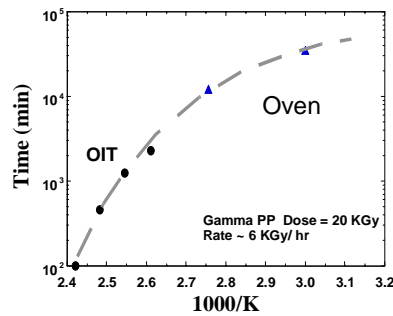


Figure 2. PP2 OIT and Oven Times.

This continuous curve behavior was very reminiscent of the data on crosslinked low-density polyethylene cable compounds studied with OIT, oxygen uptake, and oven aging experiments at the former Bell Telephone Laboratories as reported by Bair(1981). When the high temperature results were extrapolated by the Arrhenius equation to lower temperatures, grossly and physically impossible optimistic results were obtained. An examination of the activation energies revealed a more than four-fold reduction between the high temperatures and near ambient. This observation prompted the Bell lab researchers cautioning against using the high temperature OIT for low temperature durability predictions. Nevertheless, by recognizing the curvature, much more realistic predictions can indeed be produced.

### PP1 Surface Embrittlement Observation:

When an electron beam irradiated (10MeV, about 100kGy) film sample of PP1 was oven aged at 90°C, a curious phenomenon was observed. About 3 weeks into oven aging, surface fibrils orthogonal to the exposed film edge surface became visually observable. Under optical and electron microscopic observations, these fibrils are showed to be shallow, surface cracks. These cracks appeared to grow in number and their depth (measured in cross section by SEM) increases linearly as a function of time. The linear crack depth growth significantly accelerated at approximately 25% of the film thickness. The surface initiated crack propagation, and the final acceleration are strong evidence of oxygen initiated degradation with residual free radicals in the polymer bulk. At about 50% conversion, the surface area available for oxygen ingress into the bulk is no longer

limited by the original surface. Additional surface area created by the numerous cracks became dominant for the gas transport.

In a similar way the degraded layer advancing rate was determined for 70°C. In addition, a gamma irradiated (50 kGy) PP1 tensile bar was examined after 15 years of ambient storage. A layer of surface embrittled degradation product covered the entire surface, while the core of the sample remained largely intact. This observed surface degradation conforms to the diffusion limited oxidation model first proposed by Gillen and Clough (1991). The scanning electron microscopy (SEM) morphology of a high speed fracture plane (Figure 3) yielded about 80 micron thick degraded layer. From this, the surface degradation rate was determined for 25°C and plotted with other data points on Figure 4.

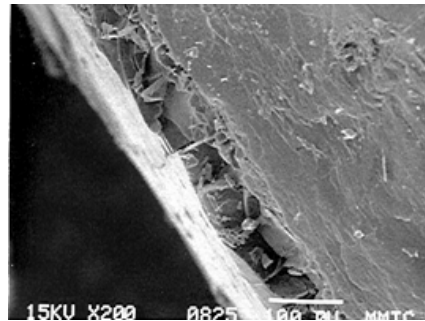


Figure 3. PP 50 KGy 15 year Storage.

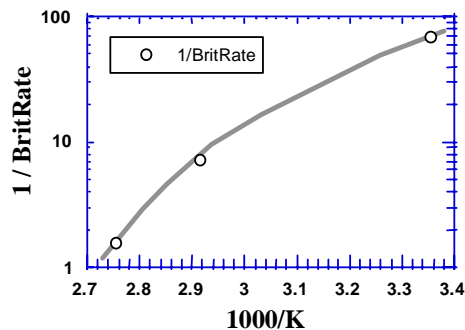


Figure 4. Surface degradation rate.

When irradiated PP1's surface degradation rates were plotted on the same Arrhenius plot, using an arbitrary 200 micron thickness (which constitutes a vertical shift) as the measure, a smooth fit was achieved with the OIT and oven aging data. However, we must note that although a smooth, continuous curve was obtained, the ambient life-time for PP1 is still somewhat uncertain because a calibration point is still lacking.

The search for a calibration point ended when several non-irradiated prototype and production PP1 bottles, which have been stored under normal laboratory conditions for up to 23 years were discovered. Since we are relatively certain of the material production stability over 20 years, this "find" allowed the calibration of our long-term durability prediction methods. When the OIT of these products were determined, an excellent linear relationship with storage time were exhibited (Figure 5 ), pointing to the zero OIT time of about 30 years. Hence, we can state, with reasonable assurance, that the durability for PP1 in the thin film form, under ambient storage, is about 30 years. When this data point was combined with all previously mentioned data in the Arrhenius form, a

continuous curve covering nearly 8 decades (100 million folds) of time was obtained. We also noted that the independently arrived lifetime of 30 years lies remarkably close (within about 25%) of the shifted ambient surface degradation rate, giving us greater confidence on its accuracy. The master curve being constructed for PP1 is therefore a compilation of all experimental data governing the lifetime of this material.

## PP1 Degradation

When various stability data of PP1 including OIT in air, surface embrittlement rates, oven ageing, OIT after gamma irradiation (at 20kGy reduces the OIT by about a factor of twenty), and OIT under 4.14 MPa of oxygen pressure were plotted on the Arrhenius form in Figure 6 , several observations becomes apparent:

- the OIT and oven aging lifetimes lie on the same continuous curve, that is, within experimental error, zero OIT or the exhaustion of the antioxidant is rapidly followed with mechanical failures,
- an additive rule appears to govern the degradation, for example, at the same temperature, durability of gamma irradiated sample under 4.14 MPa oxygen pressure can be predicted to within experimental error by the sum of the effects of gamma irradiation and high oxygen pressure measured separately,
- all curves exhibit a diminishing activation energy toward room temperature, and at the same temperature, regardless of the methodology , the slope of the curves were near identical.

This self-similarity, at least for PP1 indicates the possibility of a “master curve”, where via vertical shifts, all data can be collapsed into a single curve. This is very similar to the time-temperature superposition in rheology pioneered by Tobolsky (1962) where data at different temperatures were shifted to construct a master curve along the frequency or time axis.

## MASTER CURVE CONSTRUCTION

For PP1, by applying shift factors listed in Table 1, combined with un-shifted data from OIT in air, oven ageing, room temperature storage to 23 years, surface degraded layer advancing rate yielded one of the most complete data sets covering over 8 decades of time (Figure 7). It can be seen the local slope which is the activation energy continually diminishing from the high temperatures, and the data scatter is rarely over 25%.

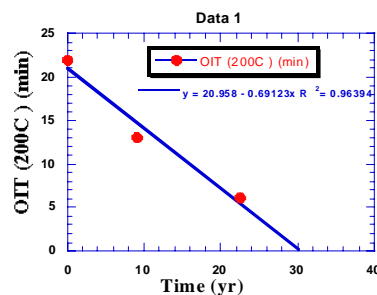


Figure 5. PP1 OIT vs. storage time.

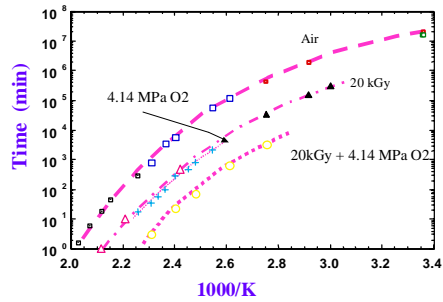


Figure 6. PP1 durabilities.

Table 1 PP1 Master Curve Data Set

Sample	Temperature Range (°C)	Shift Factor
OIT air flow 100ml/min	120-230	1
Oven Aging	110-160	1
Surface degradation rate	25-90	1*
Room Temp. Storage	25	1
4.14 MPa Oxygen OIT	120-170	25
20kGy and 4.14 MPa	90-160	210
20kGy OIT	140-180	15
20 kGy Oven Aging	60-90	15

\* The 200micron degradation thickness constitutes a vertical shift.

Likewise, the data for PP2, the radiation grade PP with hindered amine instead of the standard hindered phenol antioxidant, was also analysed. Durability measurements included OIT in air, OIT and oven stability after 20kGy gamma dose, and OIT under 4.14 MPa (600psi) oxygen pressure after 20kGy gamma irradiation. Again, when the data were shifted by a fixed factor for the given condition, a master curve covering about four and half decades of time emerges (Figure 8).

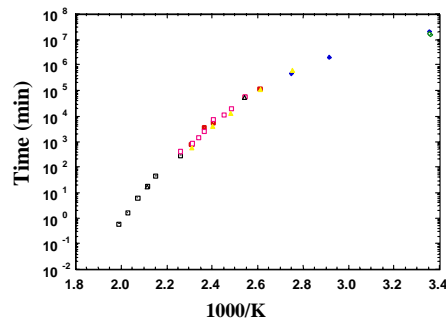


Figure 7. Master curve of PP1.

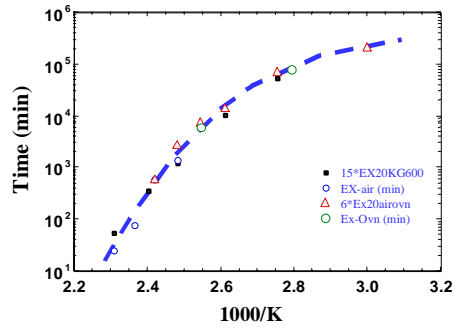


Figure 8. Master curve of PP2.

When the master curves for PP1 and PP2 and OIT data in air for PP3 were combined in the same plot, Figure 9 clearly indicates the self similarity which again justifies the construction for a master curve for all three (Figure 10). For the sake of convenience, PP1 was chosen as the reference with PP2 and PP3 shifted upward and downward respectively.

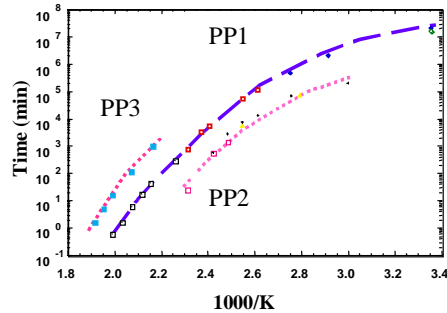


Figure 9. PP1, PP2, and OIT data of PP3.

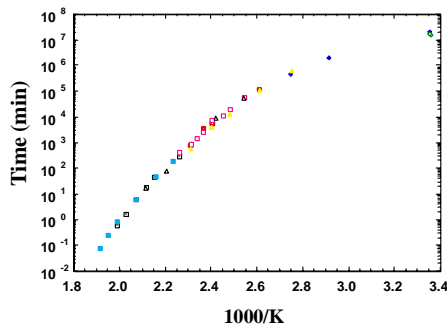


Figure 10. Master curve for PP1-3, and OPP.

Figure 10 is the master curve covering nearly nine decades of time span using vertical shift only from data sets of PP1, PP2, PP3 and limited data from the OPP film. Conditions covered included: OIT, high oxygen pressure OIT, oven ageing, ambient ageing for up to 23 years, rate of surface brittle layer formation, OIT after gamma irradiation, oven ageing after irradiation, and high oxygen pressure OIT after irradiation. The greater apparent scatter of data near 2.3 on the 1000/K scale is believed to have arisen from the PP melting points, covering both homo and copolymers. Despite the the

minor scatter, it is seen that an excellent overall matching of degradation behavior was obtained.

Also to be noted in the master curve construction, that we have made a implicit assumption, that for PP2 and PP3, although long term data are lacking, via scaling from higher temperature data, we can obtain a first order estimate of the room temperature durability. This could be the most useful aspect for the master curve.

## APPLICATION AND LIMITATION OF THE MASTER CURVE

Thus far, we have compiled data from at least four different grades of polypropylenes, spanning from homopolymers, copolymers, stabilized with phenolic antioxidant as well as hindered amine antioxidant, un-oriented sample geometry and biaxial oriented film, conformance to the master curve has been remarkable. Hence we can state with reasonable confidence, that the general functional form for PP is accurate. When the master curve was compared with available data in the literature, surprisingly good agreement has been obtained. Fore example, data from Gugamus (1989) on polypropylene thin films over 40 to 105 °C were quite comparable except a slight need for horizontal shift or temperature correction is evident (Figure 11). It is well known, in oven testing, that unless extraordinary care in calibration were taken, temperature error or intra-oven variations of 3-5°C are quite common. The horizontal shift necessary to bring our data and Gugamus' data into perfect alignment falls within this error range.

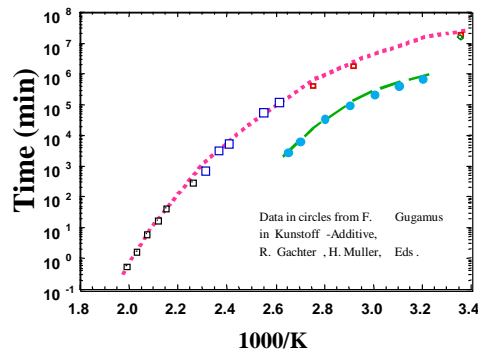


Figure 11. Data Comparison.

In this study, we have focused primarily on thin film samples, therefore, rigorously speaking, the master curve is strictly applicable only to the thin film geometry, where oxygen diffusion effects are minimized. However, since we have also measured the surface degradation rate as a function of temperature for an irradiated thick sample for up to 15 years under ambient storage, we can combine the results to estimate surface degradation layer thickness for other samples. Since polypropylene is highly notch and strain rate sensitive, we may apply the knowledge on the brittle layer thickness to simulate the presence of a sharp notch, combining with the specimen geometry and time scale of force application to predict the likelihood for ductile or brittle failure outcome. Of course, as we invoke other factors, consideration must be made for error propagation and sufficient “safety factor“ allowed for in engineering calculations.

## SUMMARY

A broad based study on the kinetics of polypropylene degradation was conducted. The Arrhenius activation energy was used as the parameter to follow the rate dependence with temperature. For most systems, a monotonic increasing trend with temperature was evident. This finding explains the frequent observation that kinetic parameters obtained at high temperatures often lead to grossly optimistic results at ambient. For a polypropylene copolymer system, combined data from OIT, oven aging and real time storage of up to 23 years, yielded one of the most complete data sets covering nearly 9 decades of time. When the activation energies from thermal processes were compared with the rate of surface embrittlement, a striking self-similarity, or near identical activation energies at the same temperature were evident. The possible existence of a master curve, when supported by further samples, could lead to further understandings on the polypropylene degradation. The additive behavior seen in many PP samples in this study could point to a way where greater predictive accuracy can be achieved in accelerated testing via ionizing radiation to substantially deplete the antioxidants or experiments under elevated oxygen pressure or both. In this way the experimental time scale can be reduced to days or weeks from years. Of course, it is always prudent to monitor samples under long term and lower temperatures for any exceptions to the master curve. The surprising low activation energies near room temperatures measured in this study also indicated that data from near ambient (e.g., 60 or 70°C) should not be extrapolated by factors significantly greater than 5 for ambient durability.

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