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RELEVANCE OF HIGH TEMPERATURE OXIDATIVE STABILITY TESTING TO LONG TERM POLYMER DURABILITY

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Abstract

In polymer degradation and durability studies, as well as predicting shelf-life for medical devices, one is confronted with the need for accurate prediction and difficulties of long term real-time evaluation. Various ways to accelerate the degradation process have met with mixed success. However, recently, in our own studies, a 'master curve' like behavior was found to be valid for polypropylene samples studied. Evidently, for samples obeying the master curve, very few data points at high temperatures can be scaled to obtain reasonably accurate estimates on long term durability.

Nevertheless, in a reference medium density polyethylene (MDPE) film material, the high temperature oxidative induction time data appear to diverge when run under air atmosphere compared with oxygen environments. In this article, we will present data on many of the polymer systems studied with an emphasis on extrapolation schemes for high temperature accelerated data to lower temperature very long-term durability. In this context, polymer and antioxidant reactivity toward oxygen, morphology, and mechanical property dependence on extent of degradation all need to be considered. And the potential and limitations of this approach will be discussed.

Keywords: oxidative stabilty test, polypropylene, polymer durability

Introduction

In addition to comparing high temperature processing stability and antioxidant formulations, another principal goal for oxidative stability studies must be the assessment and prediction of long term durability. To this end, many scientific and practical obstacles must be overcome before validity can be established. For example, many of the degradative reaction mechanisms active at higher temperatures may not be the dominant reaction pathway at lower temperatures. Morphological differences may also exist between high and low temperature conditions which may in term influence diffusion of oxygen, reaction intermediates, and altering inherent reactivity. Thus, in many studies, conclusions were reached that data at higher temperatures with the polymer in the molten state should not be extrapolated for room temperature durability prediction [1–4].

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However, in the authors laboratories, a series of polypropylenes (PP) were studied extensively, and some of them maintained at room temperature conditions for time spans of longer than twenty years. From this diverse sample set, under very different conditions, a 'master curve' appears to govern the long term durability for PP. Earlier, we have also used high temperature oxidative induction time (OIT) data from a diverse group of researchers over a very long period of time to arrive at a conservative estimate of durability on an ASTM reference material.

Hence, it is the intent of this article to critically examine the relevance and applicability of high temperature oxidative stability data toward room temperature durabilities.

Experimental

ASTM Procedure D3895 is followed in the main, except air is used instead the pure oxygen, and both the isothermal OIT and temperature scanning induction temperature were used. In addition, long term, oven aging studies was carried out in forced air circulating convection ovens at different temperatures with the oven aging time defined by visually detectable degraded zones typically near the film's free edges.

The oxidative induction test was conducted on a DuPont 1090 thermal analyzer with 910 differential scanning calorimetry (DSC) cell. The OIT is a relative measure of the degree or level of stabilization of the material tested. The specimen, typically less than 10 mg, is heated in a nitrogen environment to a preset isothermal testing temperature. Once temperature equilibrium has been established, the controller automatically switches purge gas to air or oxygen at the same purging rate. The change-over point to air or oxygen purge is taken as the zero time of the experiment. The oxidative induction stability of tested samples is assessed by monitoring an abrupt exotherm or endotherm departure from the baseline as indicated by Fig. 1 [5].

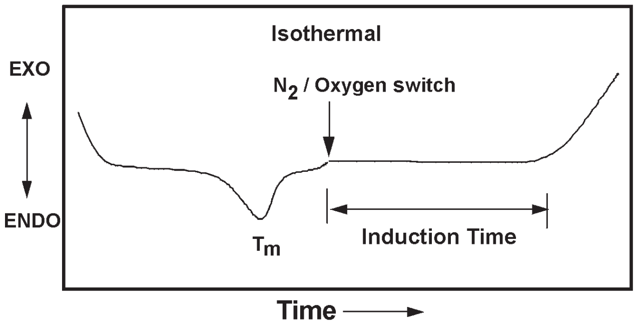

Fig. 1 OIT from DSC

For testing at elevated pressures, a TA Instruments pressure DSC cell (Model HP910) was used on a TA 910 cell base interfaced with an Instruments Specialist temperature controller based on a personal computer. Standard oxygen pressure of 4.14 MPa (600 psi) was used throughout the study. The cell was first pressurized to the designed pressure at a lower temperature and scanned rapidly to the set temperature. Time zero for the OIT was taken from the time the DSC cell achieves isothermal equilibrium at the set temperature.

To study the sample's durability under depleted antioxidant conditions, and or, increased peroxy free radical or hydroperoxide contents, we subjected the sample films to different gamma radiation doses, carried out at a commercial medical irradiation facility at dose rates approximately about 15 kGy h^{-1}.

Results and discussion

For low density polyethylene cross-linked for telephone cables, Chan *et al.* [6] attempted to estimate lower temperature durability. However, Fig. 2 shows that high

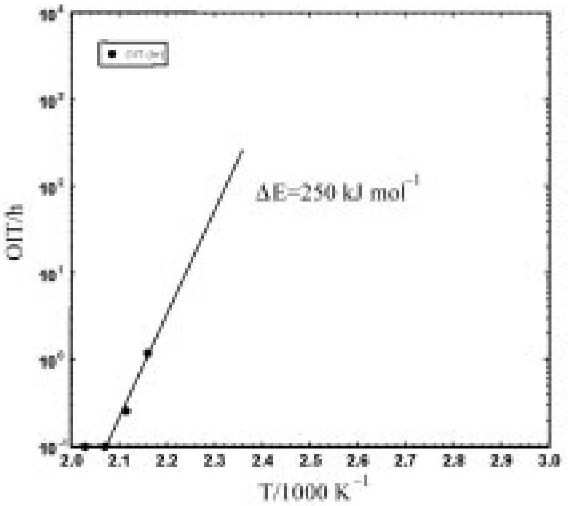

Fig. 2 LDPE activation energy

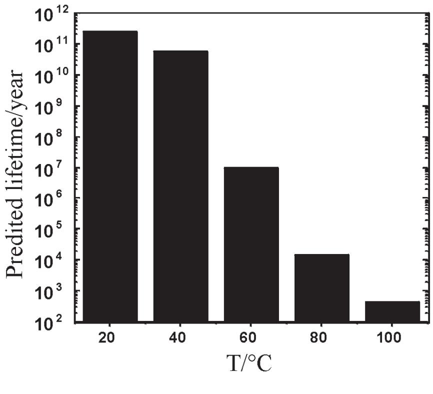

Fig. 3 Predicted lifetimes

temperature OIT followed a steep slope or activation energy of about 250 kJ mol^{-1}. When the data were extrapolated to lower temperatures, lifetimes in Fig. 3 resulted.

The predicted life times thus generated are seen as grossly erroneous. Even the nearly 400 years of predicted life-time at 100°C was glaringly contradicted by experimental data of about one year at 70°C in a circulating oven. As a result, these researchers cautioned against using the oxidative stability data at very high temperatures in the molten state to predict long term near ambient durability in the solid state.

Polypropylene master curve

We have reported earlier [7] on stability data of several polypropylenes designated as PP1, PP2 and PP3 including OIT in air, oven aging, OIT after gamma irradiation which at 20 kGy of dose reduces the OIT by about a factor of twenty, and OIT under 4.14 MPa of oxygen, 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, 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 [8] where data at different temperatures were shifted to construct a master curve along the frequency or time axis.

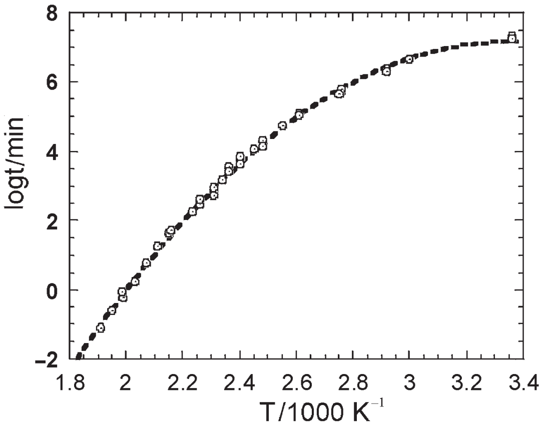

Fig. 4 Master curve for all PP samples

For PP samples studied, by applying appropriate shift factors for each data set, combined with unshifted data from OIT in air, oven aging, 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. It can be seen in Fig. 4, the local slope which is the activation energy continually diminishing from the high temperatures, and the data scatter is rarely over 25%.

The best fit for the data is:

$$\log t\ (\mathrm{min}) = -37.314 + 2.666\mathrm{e}\ 4\ (1/T(\mathrm{K})) - 3.993\mathrm{e}\ 6 (1/T(\mathrm{K}))^2 \qquad (1)$$

$$R^2 = 0.998 \qquad \text{for } 1.8 < (1/T) < 3.4$$

Figure 4 is the master curve covering nearly nine decades of time span using vertical shift only from data sets from PP1, PP2, PP3 and limited data from an 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 minor scatter, it is seen that an excellent overall matching of degradation behavior was obtained. When the master curve was compared with available data in the literature, surprisingly good agreement has been obtained. For example, data from Gugamus [9] on polypropylene thin films over 40 to 105°C were quite comparable except a slight need for horizontal shift or temperature correction is evident.

OIT and durability of a medium density polyethylene reference material

A medium density polyethylene with peak melting point of about 125°C and about 61% crystallinity has been designated as a reference material for the OIT by differential scanning calorimetry [10]. The material was stabilized by a high molecular mass hindered phenol antioxidant tetrakis-[methylene 3-(3’,5’-di-*t*-butyl-4’-hydroxyphenyl) propionate] methane, designated as AO-1 [11] and a phosphite synergist. Although Blaine *et al.* [10] has characterized the material over several years with a multitude of standard methods, their aim was primarily to establish homogeneity and lab to lab reproducibility. Due to the wide spread use of very similar materials in medical packaging, where long term shelf life storage integrity needs to be assured, and the values in understanding fundamental polymer stability, we have undertaken a study of the material over very diverse conditions, going far beyond the experimental parameters [10].

Since the flowing gas medium of air instead of oxygen was used in this study, it is necessary to compare results with that of [10]. Immediately, notable difference is seen. When plotted *vs*. the reciprocal of absolute temperature, in the Arrhenius form, the data generated in air appeared to have a significantly steeper slope, or higher activation energy than that of the oxygen. An activation energy of about 210 kJ mol^{-1} was measured for air, while only about 130 kJ was evident for oxygen. In a different medium density polyethylene system, Tikuisis and co-workers [12] obtained a best fit parameter of 125 kJ mol^{-1} between 150 and 200°C and pressures between 0.7 and 5.5 MPa (100 to 800 psi). Therefore, it appears that for the polyethylene systems studied, a significant reduction in activation energy occurred between 0.2 bar (20 KPa) and 1 bar (0.1 MPa) oxygen partial pressures.

Our own data at elevated oxygen pressures also clearly indicates that the activation energy in air, over the temperature range of 200 to 100°C, is significantly higher than that under high oxygen pressure (about 133 kJ mol^{-1} or 32 kcal). However, the high pressure data also indicates a diminishing activation energy toward ambient. The reduction in apparent activation energy with pressure was apparent in data in both [10] and studies by Tikuisis [12]. Evidently, suppression at high pressures of antioxidant volatilization must be responsible for at least part of the difference. However, a continuous shifting in the relative dominance of the degradation initiation *vs*. propagation steps, must also be responsible for contributing to the activation energies, especially over lower temperatures.

Since OIT is a kinetic parameter, and the reference material constantly degrades with time, it is difficult to state with high certainty the ultimate lifetime under ambient storage. Fortunately, through several runs of inter-laboratory testing, highly accurate data over several years are already available. From the OIT reduction with time, one can obtain an estimate of the ultimate durability. The central issue of over long times, OIT's functional dependence with time, needs to be determined. In Fig. 5, the reduction in OIT at three temperatures were plotted as a function of oven time. It is seen that in both the 90 and 70°C cases, a two-step reduction took place, and the relative height of the slow segment corresponded qualitatively to the unmelted crystalline fraction at the test temperature. A HDPE film with the same phenolic antioxidant as in ASTM-D, aged at 120°C in our laboratories also exhibited the dual slope behavior.

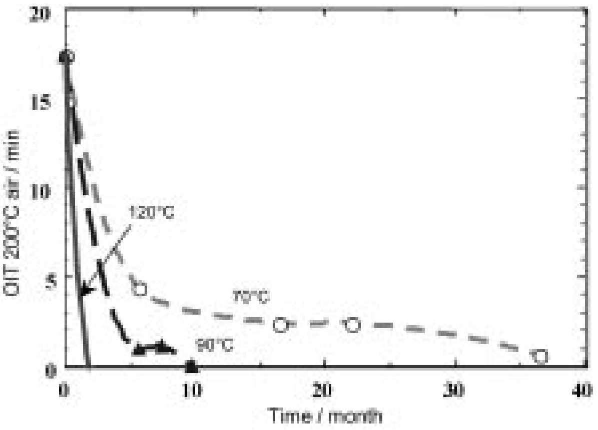

Fig. 5 ASTM-D OIT reduction with oven-time

An attractive conjecture is that the first (fast) segment describes consumption of antioxidants in the amorphous phase where the oxygen diffusion rates and concentration of antioxidants are both high. And the second segment follows slow migration of ‘trapped’ antioxidants from the crystalline domains toward the amorphous interface where reaction with oxygen takes place. Nevertheless, regardless of the actual mechanism, ample experimental evidence indicated that the linear extrapolation using the first linear segment provides a conservative lower bound for the durability.

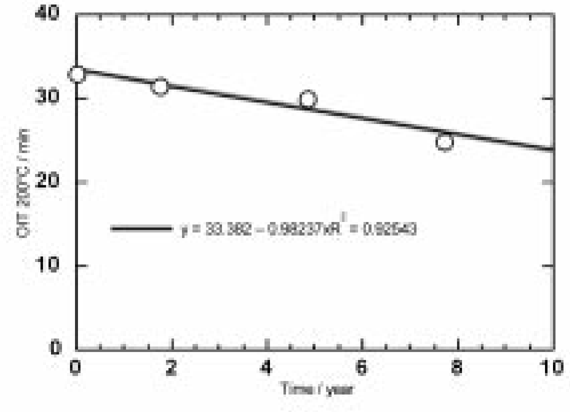

Fig. 6 OIT reduction with ambient storage

From the data in [10], a linear extrapolation indicated a zero OIT time at ambient storage of about 33 years (Fig. 6). When the 33 years lifetime is added to the Arrhenius plot of OIT and oven lifetimes in Fig. 7, a continuous curve with diminishing activation energies resulted.

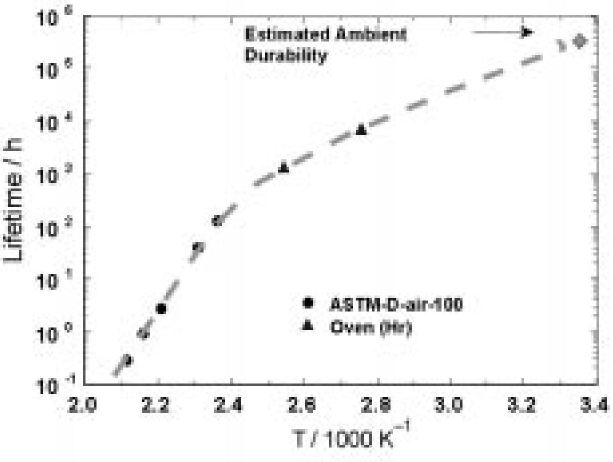

Fig. 7 ASTM-D durability

Hence, extensive data on the ASTM OIT reference material – the MDPE film designated as sample D, OIT in air appeared to better correspond to oven ageing data, and exhibit higher activation energies than in oxygen. Finally, extrapolating nearly 8 years of ambient storage data yielded a conservative estimate of shelf life of slightly over 30 years.

Comparison of PP master curve with ASTM-D

When the master curve for PP is compared with that for the ASTM reference sample D, in Fig. 8, a starting numerical similarity was apparent. Whether this is due entirely to coincidence remain to be seen. Nevertheless, the fact, that two very different polyolefins with entirely different degradation mechanisms could exhibit a near identical long-term and short-term durability behavior deserves further investigation. At a minimum, the functional shape of the curve can now be applied to a broader class of olefin polymers as a first approximation for long-term durability.

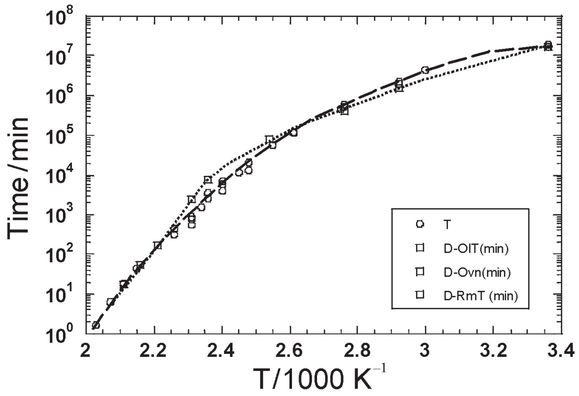

Fig. 8 Comparison PP master curve-ASTM-D

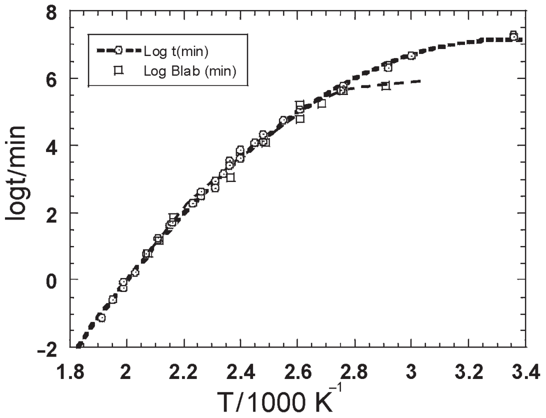

Fig. 9 PP master curve Bell Lab data comparison

Comparison between PP master curve and LDPE data

However, when the PP master curve was compared with data from the Bell Telephone Laboratories cross-linked low density cable data (Fig. 9), a serious departure at low temperatures was very evident, despite excellent agreements at higher temperatures. At around 70°C, the reported oven stability data from the Bell Lab researchers appeared to have reached a limiting plateau and little additional durability was evident at still lower temperatures. A plausible explanation for this behavior is that the antioxidant used was insufficiently permanent to allow for long-term protection at lower temperatures. In most situations, antioxidant loading exceed the equilibrium solubility at end use temperatures, thus the diffusion, exudation and eventual loss of the antioxidant become the limiting factor for durability [13]. This loss of antioxidant from the polymer matrix, at lower temperatures and long times could be one of the greatest challenges for polymer durability. This observation also offers a promising direction where through studying antioxidant loss at moderate temperatures, difficulties like that encountered by the Bell Labs researchers can be overcome and much better long-term predictions achieved.

Summary

Through comparison of numerous polyolefin data sets: PP, MDPE, and LDPE, one conclusion is clear, that high temperature OIT data can not be extrapolated in a linear fashion for the low temperature durability. At a minimum, the curvature on the log durability time *vs*. ($1/T$) must be taken into account. It was noted that at near room temperatures, the durability function frequently exhibited very low apparent activation energies. In other words, only very modest acceleration in aging can be achieved by moderate elevation in temperature.

If the antioxidant formulation has adequate solubility in the matrix, and via molecular mass or other means, the outward diffusion from the polymer can be minimized, the extrapolation via the curved master curves could be a good model for initial durability estimates. To insure long-term stability, actual monitoring of the antioxidant migration and exudation should be carried out at moderate temperatures.

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