Polymer durability estimates based on apparent activation energies for thermal oxidative degradation

Samuel Ding[*], Atul Khare, Michael T.K. Ling, Craig Sandford, Lecon Woo

Corporate Research and Technical Services, Baxter International, Round Lake, IL 60073-0490, USA

Abstract

In order to further our understanding of polymer durability, the degradation kinetics of a series of polymers was studied. The Arrhenius activation energy was used as the parameter to follow the rate dependence as a function of temperature. For most systems, it was evident that the apparent activation energies increase monotonically with temperature. This finding explains the frequent observation that kinetic parameters obtained at high temperatures often lead to grossly optimistic estimates of shelf life at ambient conditions. The activation energies of polypropylene from the surface embrittlement processes were also found to have a striking similarity to the thermal processes, with nearly identical activation energies at the same temperature. A good understanding of this observation could lead to broader applications and further the understanding of polymer degradation. © 2001 Published by Elsevier Science B.V.

1. Introduction

Few universally valid predictive methods exist for the study of polymer degradation and durability over wide spans of temperature and time. Many of the high temperature "accelerated" oven tests have been deemed unrealistic for evaluating several prominent degradation modes. In the mean time, for practical reasons, experimental time spans of much longer than a year are extremely difficult to manage. In the medical plastics industry, products are frequently sterilized by ionizing radiation, which severely depletes the antioxidant package. Yet to conform to many regulatory requirements, a scientifically based

estimate of post irradiation shelf life must be provided. Thus, a better understanding on the time and temperature influence on the material's performance is a necessity for product introduction.

Frequently, degradation reactions are temperature dependent. The rate constant k can be expressed in the Arrhenius form:

$$k = k_0 \exp\left(\frac{-\Delta E}{RT}\right) \qquad (1)$$

where k_0 is the pre-exponential factor, ΔE the activation energy of reaction, R the gas constant, and T the absolute temperature in degrees Kelvin. The activation energy can be obtained from the slope of log k against $1/T$.

In this study we have examined the Arrhenius activation energy as a function of temperature for many polymer systems important in the medical

* Corresponding author.
E-mail address: ding@baxter.com (S. Ding).

industry. Data from oxidative induction time (OIT), accelerated oven aging, and real time ambient storage for up to 23 years was used to determine the functional behavior and quantitative significance of the calculated activation energy.

2. Experimental and materials

Methods used in this study include ASTM D3895-92 isothermal oxidative induction time (OIT) conducted using a DuPont 910 differential scanning calorimetry (DSC) cell controlled by an Instrument Specialist temperature controller. Forced convection air circulating ovens were used at various temperatures to assess long-term oven age shelf life with sample embrittlement as endpoints. Morphological studies were done with a Reichert FC4E cryoultramicrotome to prepare undistorted material blocks for scanning electron microscopy (SEM) analysis. SEM observations were conducted either with a JEOL 6300 FESEM or a JOEL 35CF electron microscope after sputter coating with palladium for surface conductivity. Materials studied included polypropylene (PP), high density polyethylene (HDPE), low density polyethylene (LDPE), ethylene propylene diene rubber (EPDM) and polyester–ether thermoplastic elastomers. To assess effects of ionizing radiation, gamma exposure at various doses was conducted in a laboratory gamma cell at dose rates of approximately 6–10 kGy/h.

3. Results and discussion

For the materials identified above, both OIT and Chemi-luminescence data support the general mode of degradation in which primary alkyl radicals are generated as a consequence of atmospheric oxygen diffusing into the polymer to form peroxy and hydroperoxy radicals (Fig. 1). The rate limiting steps in this complex chain reaction scheme determine the overall degradation rate. In this regard, stabilizers, such as phenolic antioxidants and their phosphite synergist, interrupt the degradation cycle by eliminating organic radicals, or by decomposing hydroperoxides, and are sacrificially consumed in the process. The activation energy of the degradation, as expressed in the Arrhenius form, will be affected by factors such as polymer composition, stabilizer package, and polymer morphology.

3.1. Gamma radiated polypropylene

Catastrophic failures have been reported during the PP shelf life storage period. Intense investigation has led to the hypothesis that long lived 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 [1,2]. When sufficient number of the tie molecules between crystallites are cut through this chain scission process, PP's elongation is reduced dramatically and catastrophic failures follow.

To establish that long lived radicals do play a significant role in post irradiation PP degradation, a PP film sample was examined by electron paramagnetic resonance (EPR) spectroscopy. A distinct free radical spectrum was detected at room temperature about 6 months after irradiation. Incidentally, the strong EPR signal was completely eliminated when the sample was annealed in a vacuum oven at 90°C, a
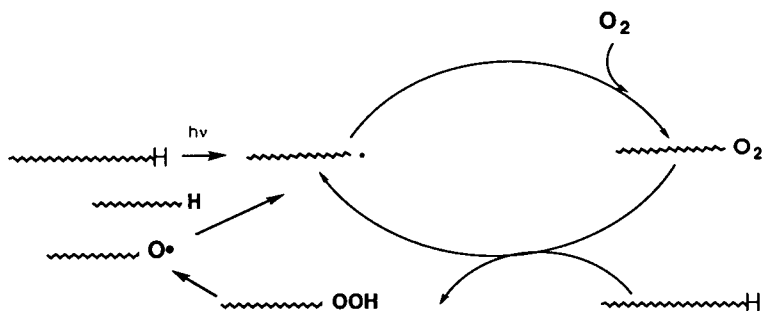

Fig. 1. Oxidative kinetic chain reaction for the degradation of polyolefins.

temperature much above the glass transition for the amorphous phase for PP, and well into the alpha relaxation for the crystalline phase of PP [3].

In a separate study, the OIT of a radiation grade PP was determined under air flow conditions of 100 ml/min and the result compared with the same film sample (about 130 µm in thickness) after 20 kGy of gamma exposure at about 6 kGy/h dose rate. To access lower temperature thermal stability, 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 OIT and oven failure times for the gamma irradiated samples were plotted onto the Arrhenius plot, a continuous curve with diminishing slope toward lower temperatures emerged (Fig. 2). This kind of continuity of functional behavior of OIT data at higher temperatures and oven stability data closer to ambient could, at least in principle, produce long-term property prediction based on OIT data, provided that the rate of slope change can be determined separately.

3.2. Low density polyethylene

Data for the degradation of the irradiated PP was very reminiscent of crosslinked low density polyethylene cable compounds studied with OIT, oxygen uptake, and oven aging experiments at the former Bell Telephone Laboratories [4] (Fig. 3). When the high temperature results were extrapolated using the Arrhenius equation to lower temperatures, grossly optimistic and physically impossible results were obtained. An examination of the activation energies
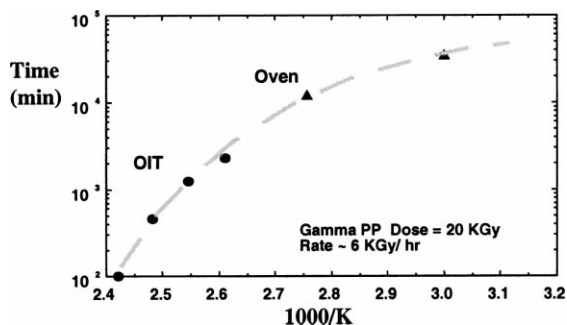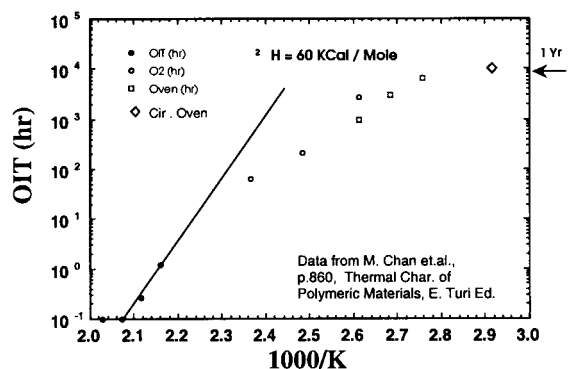
Fig. 3. Temperature dependence for oxidative induction times and oven failure times for low density polyethylene.

indicated a more than fourfold difference between the high temperature and near room temperatures values (Fig. 4). This observation prompted a caution against using high temperature OIT data for low temperature durability predictions. Nevertheless, by recognizing the curved nature of the durability function, realistic predictions can indeed be achieved.

3.3. EPDM rubber

A class of thermoplastic elastomers are created when olefinic polymers (polyethylene, polypropylene) are dynamically vulcanized with a crosslinkable elastomer such as ethylene propylene diene rubber (EPDM). These so-called thermoplastic vulcanizes are quite resistant to oxidation and studies of their long-term stability have been carried out [5]. A general-purpose thermoplastic sample of 50 Shore D hardness was chosen for the OIT study. Published

Fig. 2. Oxidative induction times and oven failure times as a function of temperature for polypropylene subjected to gamma radiation.
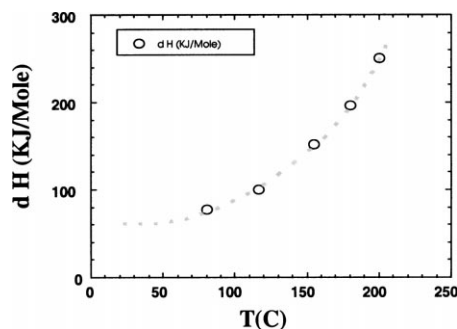
Fig. 4. LDPE activation energies derived from data in Fig. 3.
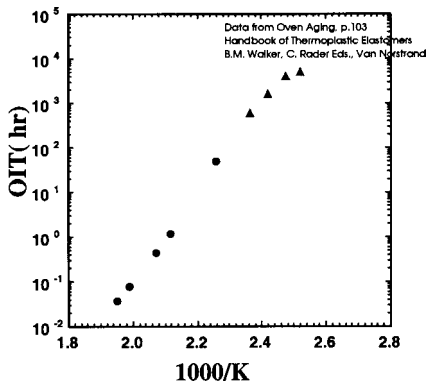
Fig. 5. Temperature dependence of oxidative induction times and oven failure times for EPDM.

Fig. 7. Temperature dependence of oxidative induction times and oven failure times for polyester thermoplastic elastomer.

data from a long-term oven aging study for 50% strength reduction was plotted on the same graph for comparison (Fig. 5). The activation energies at several temperatures are plotted in Fig. 6. It is seen that at temperatures well over 100°C, the activation energy for oxidative degradation has already decreased to about 80 kJ/mol. Thus, only modest extensions in lifetime can be expected with further reduction in temperature.

3.4. Polyester elastomer

Polyester thermoplastic elastomers (TPE) based on polybutylene terephthalate (PBT) hard segment and tetramethylene ether (PTMO) soft segments constitute an important class of medical elastomers because of their wide property range, solvent bonding capability, oxidative stability and processing ease.
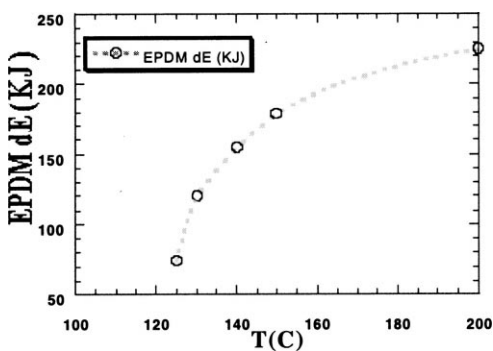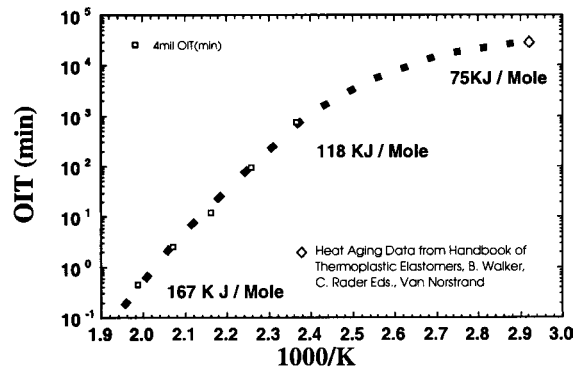
OIT measurements conducted in air at higher temperatures again coincided with the oven aging data reported in the literature (Fig. 7). The activation energies at several temperatures were also calculated.

3.5. PP surface embrittlement

For an electron beam irradiated PP film sample 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 observation, these fibrils are shown to be shallow, surface cracks (Fig. 8). These cracks appeared to grow in number and their depth (measured in cross-section by SEM) increases linearly as a

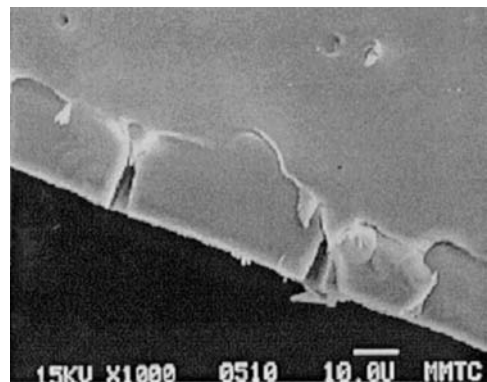Fig. 6. EPDM activation energies derived from data in Fig. 5.

Fig. 8. Electron micrograph of degrading poly(propylene) surface showing crack formation.
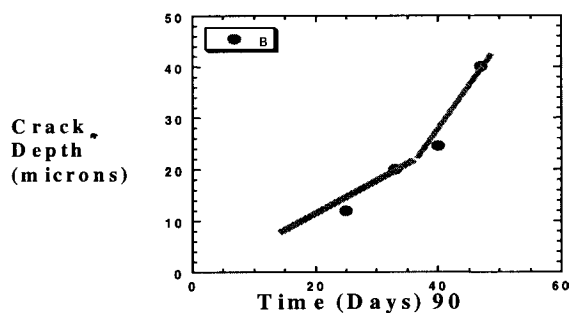
Fig. 9. Crack depth as a function of time for poly(propylene) aged at 90°C.

Fig. 10. Temperature dependence for oxidative induction times, oven failure times, and real time failure for poly(propylene).

function of time. The linear crack depth growth significantly accelerated at approximately 25% of the film thickness (or about 50% of the film volume) (Fig. 9). The activation energies determined from the rate of surface embrittlement are:

Temperature (°C)	30	70	90
E_a (kJ/mol)	33	58	82

The very low activation energy measured by the surface embrittlement rates shows that modest extension in lifetime prediction can be expected from "accelerated tests" conducted at moderate temperatures such as 60–70°C to those obtained at room temperature.

3.6. Activation energy for poly(propylene) aging from OIT, oven aging and real time aging

Recently, in the authors' laboratories, several prototype and production polypropylene bottles, which have been stored under ambient conditions for up to 23 years, were discovered. This "find" could allow the calibration of long-term durability prediction methods. When the OIT of these products were determined, an excellent linear relationship with storage time was observed, pointing to the zero OIT time of about 30 years. Hence, we can state, with reasonable assurance, that the durability of this particular grade of PP in the thin film form, under ambient storage, is about 30 years. When this data was combined with newly generated OIT and oven life data, plotted in the Arrhenius form, a continuous curve covering nearly 8 decades (100 million folds) of time was obtained (Fig. 10). When the local slopes were measured and
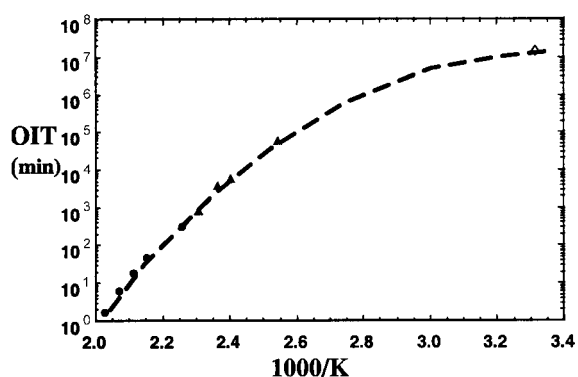
converted to the activation energy at various temperatures, again, a concave curve resulted.

Yet another significant observation on PP is that when the activation energy from thermal aging processes is compared with the activation energies for brittle layer formation, near identical results are obtained. This apparent "self-similarity", or near identical activation energies at the same temperature exhibited for different degradation measurement parameters and different grades of polypropylene, could lead to much simplified modeling and understanding of the degradation and durability process. Efforts are currently underway to gather more supporting data for this self-similarity and the utility it could provide.

4. Summary

In an effort to further understand polymer durability, a broad-based study of the kinetics of polymer 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 predictions for behavior at ambient. Compared to the commonly applied "photographer's rule" of twofold increases in reaction rates for every 10°C rise in temperature, which at near room temperatures, implies an activation energy of about 55 kJ/mol, activation energies well under

50 kJ/mol have been measured. The small magnitude of the activation energies indicates that only modest "acceleration" could be obtained during moderate temperature aging. 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 over 8 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. This observation could lead to broader applications and further understandings of the polymer degradation.

References

[1] G.N. Foster, in: J. Pospisil, P. Klemchuk (Eds.), Oxidation Inhibition in Organic Materials, Vol. 2, CRC Press, Boca Raton, 1989.

[2] L. Matisova-Rychla, J. Rychly, in: R. Clough, N. Billingham, K. Gillen (Eds.), Polymer Durability, American Chemical Society, Washington, DC, 1996.

[3] L. Woo, J. Palomo, T.K. Ling, E. Chan, C. Sandford, Med. Plastics Biomater. 3 (2) (1996) 36.

[4] H.E. Bair, in: E. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981, p. 869.

[5] N.R. Legge, G. Holden, H.E. Schroeder (Eds.), Thermoplastic Elastomers, Macmillan, New York, 1987.