

Application of the oxidative induction test to depolymerizing systems

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Abstract

Since the development of the oxidative induction time (OIT) test by former Bell Telephone Laboratories researchers, there have been many studies to broaden its applicability to polymers beyond the original polyolefins. The basic premise in OIT studies is that a detectable oxidation onset is based on the differential reactivity between the polymer matrix and free radical scavenging antioxidants like hindered phenols. This situation does not exist in depolymerizing systems such as polymethylmethacrylates (PMMA), so many researchers concluded that a correlation did not exist for these systems. We will report on the observation of a clear cut, Arrhenius-like oxidative induction time behavior in a toughened PMMA system with high pressure DSC. The relationship between the observed OIT at elevated temperatures and high oxygen pressures with lower temperature oven aging studies will be presented. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The oxidative induction time (OIT) test was developed by former Bell Telephone Laboratories researchers as a rapid screening test for the relative effectiveness of stabilizer packages for olefinic cable jackets. Later, it was discovered that due mainly to the curvature in the Arrhenius activation energy plots, gross over-estimates of near room temperature lifetimes were encountered. However, it is generally accepted that the product lifetime corresponded closely with the residual antioxidant content. That is, when the antioxidant was consumed or had disappeared from the polymer matrix, the polymer

degraded very rapidly and mechanical failure soon ensued. However, for non-olefinic polymers, especially those with relatively low ceiling temperatures, and which depolymerize at high temperatures, there has been little indication that OIT can be measured, or that it can be used to relate to real time durability. In fact, some earlier work indicated there is no correlation between OIT and the onset of degradation [1].

2. Experimental

A toughened transparent injection molding grade polymethylmethacrylate (PMMA) was used in this study. A TA Instruments 910 DSC cell or a pressure DSC cell was used with an Instrument Specialists controller. Both temperature scanning and isothermal modes were used. For low-pressure operations, air

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purge with flow rate of 100 ml/min was used instead of the oxygen atmosphere specified in the ASTM 3895-92 procedure [2]. For the pressure DSC, a constant oxygen pressure of 400 psi (2.8 MPa) was used at various temperatures. To compare relative oxidative stability after sterilization with ionizing radiation, both gamma and electron beam irradiation were used at doses up to 90 kGy. As is usually the case, the electron beam irradiation dose rate was about 3–4 orders of magnitude higher than that of the gamma. For oven aging studies, flat specimens were prepared from injection molded devices and sectioned into rectangular pieces approximately 3 mm wide \times 1 mm thick and about 25 mm in length. After aging in circulating ovens for specified periods, ductility was determined by a rapid 90° bend with long nosed pliers. The failure time was taken as the onset of brittle failure and failure morphologies characterized with brittle, glassy failure planes.

3. Results and discussion

The schematic oxidative degradation reaction mechanism for hydrocarbons is depicted in Fig. 1. It is seen that a catalytic propagation and free radical formation cascade resulted from a single initiation event. In this scenario, the traditional hindered phenol type antioxidants function as free radical scavengers or hydrogen donors to interrupt the propagation cycle. However, this mode of protection is not expected to function unless the antioxidants are much more reactive than the polymer matrix. With depolymerization type polymers like PMMA, this mode of action is not expected.

However, under high oxygen pressures (2.8 MPa/400 psi), PMMA exhibited a clean, distinct OIT onset

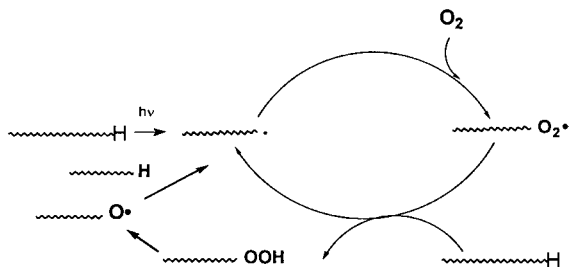


Fig. 1. Schematic illustrating polymer thermal oxidation reactions.

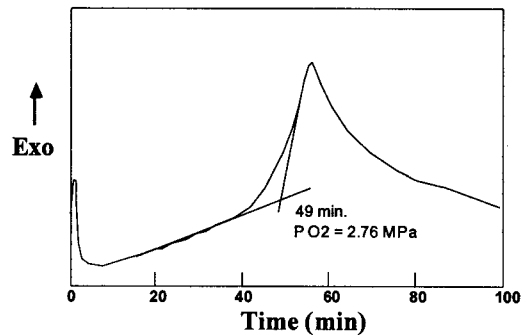


Fig. 2. PMMA OIT event at oxygen pressure of 2.76 MPa.

at about 49 min (Fig. 2). This corresponds to a temperature of about 140°C. When the OIT times were plotted in the Arrhenius form against the reciprocal absolute temperature, a gently curving dependence was obtained, with the higher temperature segment exhibiting an activation energy of about 160 kJ mol⁻¹ (Fig. 3).

The effect of different radiation types and doses on the OIT of PMMA is shown in Fig. 4. It is clear that a 2.5 MRad (25 kGy) gamma dose resulted in a significant OIT reduction. Further gamma irradiation appeared to have only a small effect. This observation suggests the presence of dissolved oxygen in the sample prior to irradiation and minimal oxygen ingress during the irradiation process.

Gamma-irradiated PMMA (25 kGy) was aged in an oven at 120°C. The OIT was measured under oxygen pressure periodically. It was found that the OIT

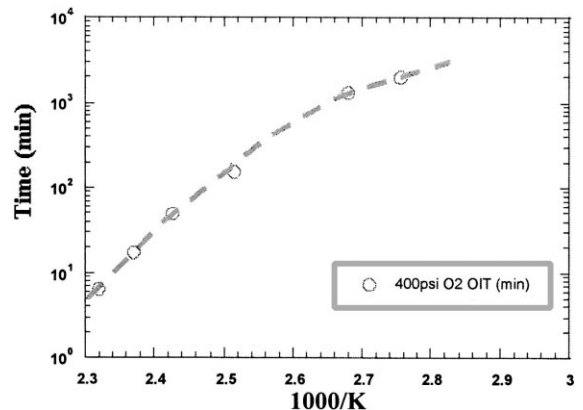


Fig. 3. OIT Arrhenius plot of PMMA under 400 psi oxygen pressure.

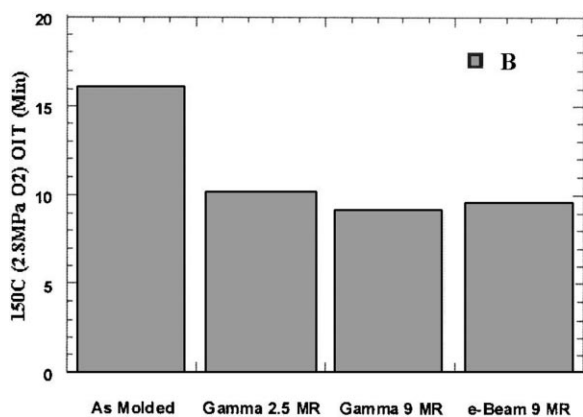


Fig. 4. Effect of gamma and e-beam irradiation on the OIT of PMMA.

remained constant up to about 100 h, and did not fall to near zero until after 400 h (Fig. 5).

This is in contrast with polyolefin systems where the OIT measured in air coincides and matched that of the oven failure times [3] (Fig. 6). What we seemed to observe is that both the OIT and oven aging followed a similar temperature dependence, and yet the oven aging and OIT endpoints appeared to follow entirely different pathways. In oven aging, the sample becomes brittle after about 130 h at 120°C and yet their OIT appeared to persist above $\frac{2}{3}$ of the original value to nearly 400 h. This is a strong indication that a heterogeneous reaction is involved where the mechanical property and chemical reactivity followed different endpoints. Some of the possibilities for the heterogeneous reactivity are: (1) sample surface and

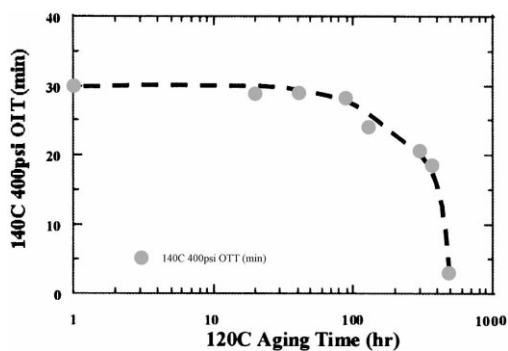


Fig. 5. OIT for gamma-irradiated (25 kGy) PMMA as a function of oven aging time at 120°C.

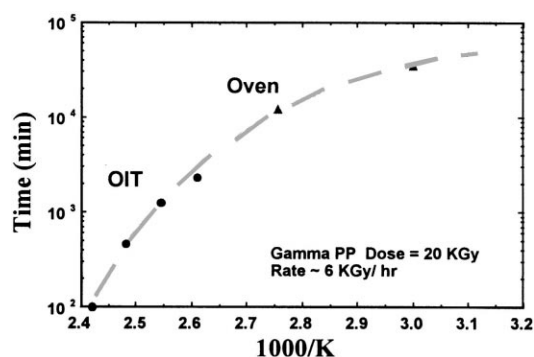


Fig. 6. Semilog plot of OIT against $1/T$ for radiation grade PP.

bulk reacting differently due to oxygen diffusion effects; (2) on a microscale, the rubber particle domains or their interface could react differently from the surrounding matrix. Of course, the possibility also exists for a combination of both pathways.

One model consistent with the above observation is that antioxidant-like species are located primarily near the impact modifier rubber particles dispersed in the brittle matrix. For the material to exhibit brittle failure, all that is required is the destruction of a small fraction of the impact modifier, especially that located near the rubber-matrix interface. In other words, the OIT and the oven aging ductility degradation are both governed by the effectiveness of antioxidant species. While the OIT measures the endpoint, the ductility depends on spatially localized oxygen consumption, which could occur at a much earlier stage. This contrasts sharply with the polyolefin systems, where depletion of the antioxidants typically precedes the embrittlement slightly. In our case, the brittle onset appears at about one third to one quarter of the OIT. Hence, to be able to relate the OIT observations at elevated temperature and pressures to oven storage, additional experiments are required.

Further experiments on gamma sterilized samples appears to exhibit a two step OIT response. After the initial temperature equilibrium was established, a clearly discernable exothermic plateau seemed to exist before the final, much more intense OIT event (Fig. 7). The intensity or the height of the first exothermic plateau also increases with oven aging at 120°C (Fig. 8). To monitor the progress on the oven aging, the ratio of the height of the OIT peak to that of the first plateau (R) is plotted in Fig. 9. It is seen that

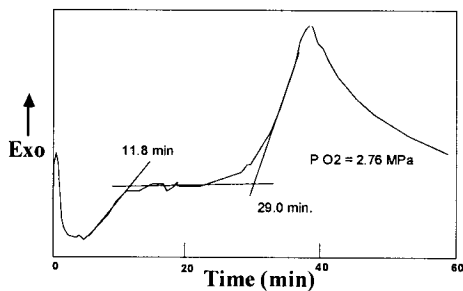


Fig. 7. Thermal behavior showing oxidative kick-off for gamma-irradiated (25 kGy) PMMA which was oven aged for 20 h at 120°C.

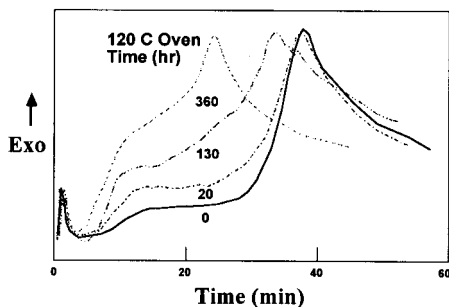


Fig. 8. Thermal behavior showing oxidative kick-off for gamma-irradiated (25 kGy) PMMA which was oven aged for different times at 120°C.

immediately after gamma dose of about 25 kGy, the plateau becomes visible with a measurable height ratio R . During the initial aging period, a slight rise in the ratio is observed, before a final dramatic rise at about

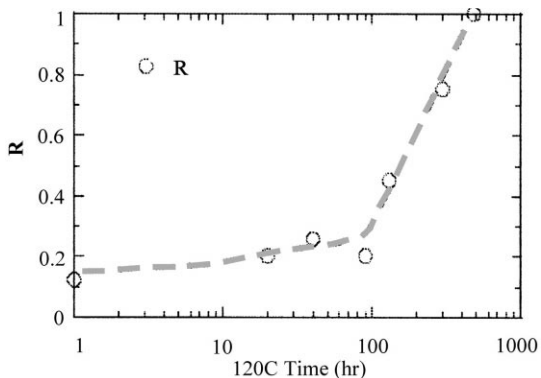


Fig. 9. Plot of ratio R (height of OIT peak/height of OIT peak for no oven aging) against the oven aging time at 120°C for gamma-irradiated (25 kGy) PMMA.

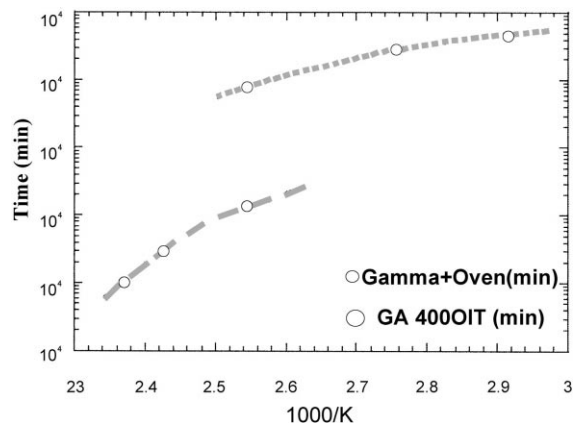


Fig. 10. Plot of OIT (400 psi O_2 pressure) and failure based on oven aging time (at 120°C) against $1/T$ for gamma-irradiated (25 kGy OIT) PMMA.

100 h. Of course, we expect the oven aging OIT functional behavior to be somehow related to the morphological makeup and their oxidative behaviors.

It is interesting to note that the onset for R corresponded closely to that of the oven aging lifetime. In other words, when the plateau begins to gain significant intensity compared to the main oxidation event, mechanical ductility is lost. This contrasts sharply with olefin systems where brittleness is typically observed at the zero OIT point. Another aspect requiring consideration is that in the semicrystalline olefin systems, antioxidants are distributed predominantly in the continuous amorphous phase while the impact toughened PMMA system the rubber phase is dispersed discontinuously in the rigid matrix.

When the OIT under 2.8 MPa (400 psi) oxygen pressure were plotted with the oven aging times for the gamma-irradiated samples, nearly a 2-decade difference separated the two sets of data, as seen in Fig. 10. Hence, elevated oxygen pressure caused about a 100-fold acceleration in degradation.

To understand the 2-decade separation between high oxygen pressure OIT and oven aging times, a pressure dependence study was carried out at 140°C. As shown in Figs. 11 and 12, a very linear intensity (peak height of the OIT event in mW) with oxygen pressure was obtained. The intensity dependence with oxygen pressure explains the difficulty for low or atmospheric pressure detection for the OIT event, since at lower oxygen partial pressures, very poor

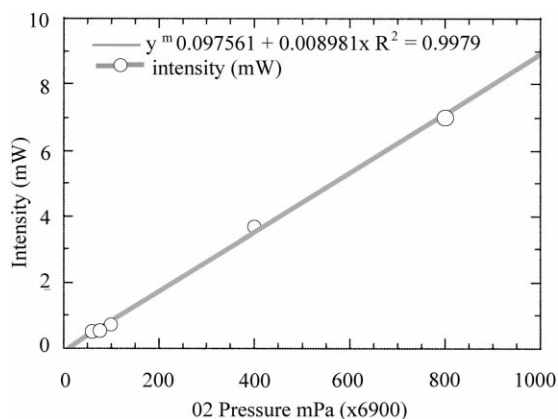


Fig. 11. The intensity or height of the oxidative kick-off plateau against oxygen pressure.

signal to noise ratio (S/N) was encountered. However, the usual $1/OIT$ versus the square root of pressure yielded ambiguous results at low oxygen pressures; instead of steady increases in OIT with reduction in oxygen pressure, either a limiting value or an upturn in $1/OIT$ values was observed. This indicates that in addition to S/N ratios, there may be mechanistic differences between reactions at different oxygen pressures.

To confirm the observation that during oven aging, the brittleness onset occurs at about three or four times earlier than the OIT disappearance, a reverse experiment was carried out. Using the pressure DSC cell, pre-cut samples approximately 4 mm in width and 1 mm in thickness were conditioned at 120°C and 2.8 MPa (400 psi) oxygen pressure, and samples

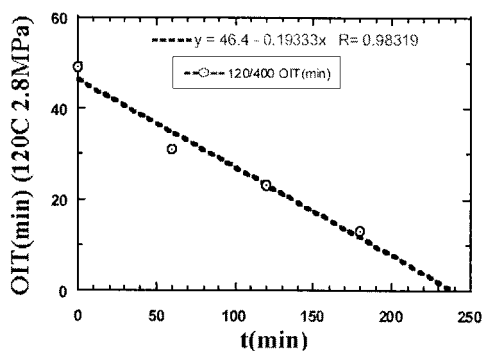


Fig. 12. OIT reduction after 120°C as a function of 2.8 MPa O_2 storage time.

withdrawn at different time intervals for brittleness tests described earlier. In this experiment, brittleness was observed between conditioning times of between 100 and 140 min. The OIT onset under the same conditions was measured as 230 min, confirming the previous observation that brittleness preceded the OIT. Also, samples conditioned under the 120°C and 2.8 MPa at various times appear to exhibit a linear reduction in OIT with an x -axis intercept of about 235 min, in excellent agreement with the measured 230 min (Fig. 12). Thus the remaining OIT and conditioning history appeared to follow zero-order kinetics. Once again, the sample brittleness was observed at a fraction of the OIT time, lending support to the heterogeneous reaction model.

Currently we are studying the sample history dependence and the significance of this minor early event.

4. Morphology

In an oven aged 25 kGy sample exhibiting brittle failure after 300 h at 120°C , the failure surface was subjected to detailed scanning electron microscopic analysis. It is seen in Fig. 13, under moderate magnification, a very thin ($\sim 30\ \mu\text{m}$) very brittle layer appeared to cover both surfaces. However, the fracture morphology across the sample thickness seemed to exhibit two distinct modes of fracture propagation. On the left-hand side, brittle, glassy failure morphologies

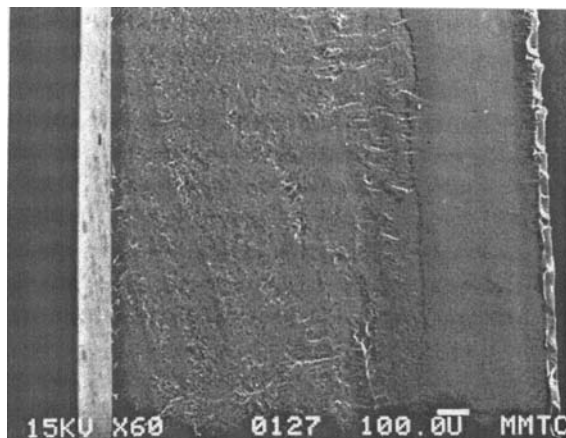


Fig. 13. Brittle sample morphology.

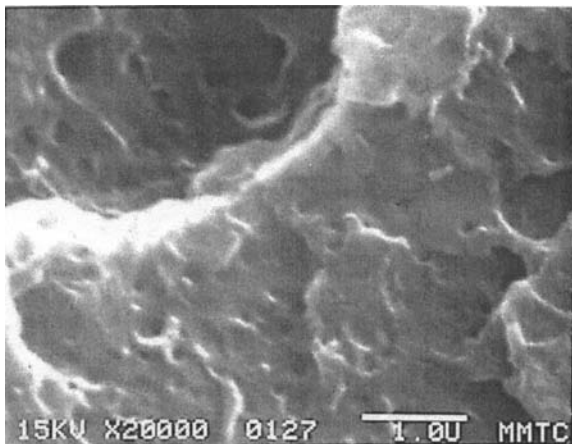


Fig. 14. Brittle morphology.

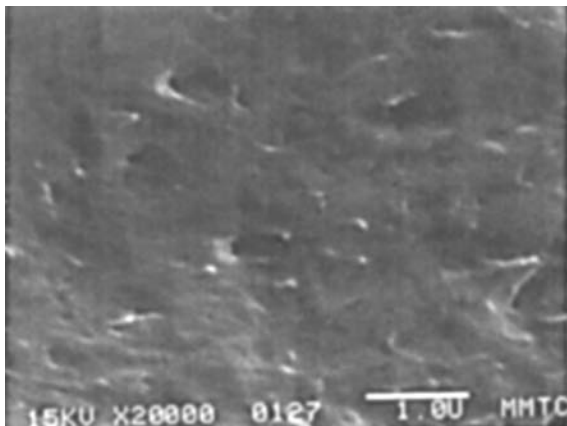


Fig. 15. Ductile morphology.

dominated, while at about 60% of the thickness, the morphology changes abruptly into a milky, ductile mode of propagation. The initiation side (left) is characteristic of fast crack propagation under high strain rates, and the right hand 40% of the surface is typical of a rubber toughened failure mode. The milky

appearance is the result of volume dilatation effects from craze initiation from the rubber particles which dissipate the fracture energy. Under much higher magnifications (Figs. 14 and 15) the brittle morphology is seen as glassy planes with numerous cavities about 100–300 nm in diameter where the rubber particles have been cleanly separated from the matrix. In contrast, the ductile zone under higher magnification clearly shows large scale yielding and retraction remnants from craze fibrils near the rubber particles.

From the microscopic observations, it appears that a combination of surface to bulk behavior and micro-mechanical behavior differences are responsible for the observed brittle failures.

5. Summary

An unambiguous OIT event was observed under elevated oxygen pressure for an impact toughened PMMA material, contrary to expectations that for depolymerizing systems, OIT are not observable. The intensity of the event depends strongly on oxygen pressure, leading to very poor signal to noise ratios and data quality at atmospheric pressures. The observed event also shows complex dependence on oven aging. A plausible model attributing the OIT originating from preferentially oxidizing compounds at or near the rubber domain interface was proposed.

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