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Application and limitations on thermal and spectroscopic methods for shelf-life prediction

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Abstract

In medical products, shelf-life after thermoplastic processing and sterilization is important, and ionizing radiation has become a preferred sterilization mode for medical devices. We have employed successfully thermal analytical methods to predict shelf-life for many polyolefin materials. However, as the material of construction becoming more sophisticated: multiphase alloys and blends, multi-layer constructions, etc., issues existed that require clarification as to what extent these methodologies are applicable.

We have employed thermal analytical methods in conjunction with other spectroscopic and morphological methods to study the applicability and limitation of these techniques. Results combined with real life and simulated aging experiments will be presented in this article.

Keywords: OIT; Heterogeneous; FTIR; Degradation

1. Introduction

Earlier, we have provisionally established that there is a master curve prescribing the thermal oxidative degradation of polyolefins, especially polypropylene [1–5]. The master curve was constructed by plotting the oxidative induction times in air (OIT), oven aging failure times, and rate of surface brittle layer formation in the Arrhenius fashion, and through the self-similarity of the entire family of curves and application of vertical shifting to arrive at a single curve with little scatter. The implication of the master curve and acceptability of the vertical shifting scheme, is that methods that greatly accelerate the thermal oxidative process, e.g., irradiation with ionizing radiation, OIT in elevated oxidative atmosphere pressures, can be scientifically integrated to generate data in very short time scales. Reasonably reliable estimates on room temperature shelf-life can be generated via the established master curve and the measured vertical shift factor without observations lasting decades of time.

In this article, an alloy of radiation grade polypropylene and ultra low density polyethylene (ULDPE) impact modifier was studied in detail to test the applicability of the master curve methodology to multi-phase systems.

2. Experimental

The polypropylene used was a medical radiation grade copolymer of 25 melt flow, and the ultra low density polyethylene was about 0.90 density. Sample of the PP/ ULDPE blend in 80/20 ratio was injection molded into relatively thick (about 1.2 mm) specimens. Irradiation dose at about 40 KGy was conducted on an electron beam facility at about 10 MeV energy. Sections of the sample were prepared and subjected to oven aging at multiple temperatures. Samples withdrawn at various time intervals were subjected to the OIT analysis [6] in open aluminum pans and air flow rate of 100 ml/min. For selected samples, a serial sectioning of about 30 μm in thickness was carried out parallel to the sample surface with a Reichert microtome and Fourier transform infrared (FTIR) transmission spectra acquired on a Matson FTIR spectrometer fitted with a aperture disk of about 7 mm diameter to accommodate the small sample sections. From the FTIR data, the ratio of absorbance peak heights at 1710 cm^{-1} (carbonyl) and about 900 cm^{-1} (PP) was used to quantify the degree of degradation.

3. Results and discussion

Data from reference [1] of the master curve construction for PP1 a widely used medical grade polypropylene and the master curves are presented in Fig. 1. Clearly, the self-similarity of data justified the vertical shift procedure for the master curve (Fig. 2)

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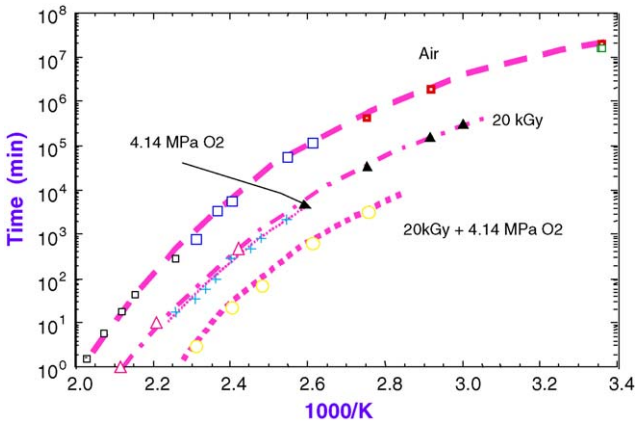

Fig. 1. Master curve construction for PP1 from ref. [1].

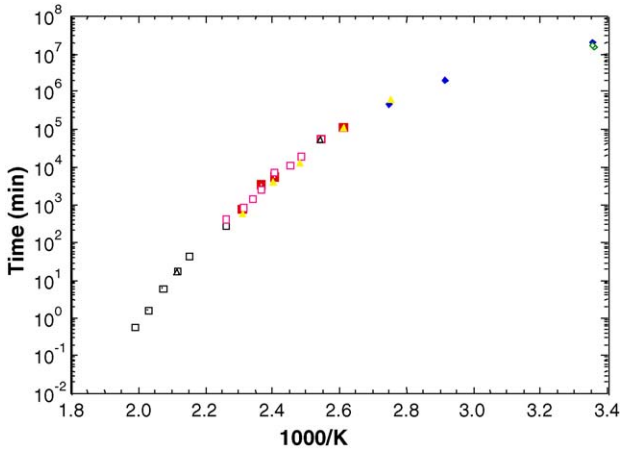

Fig. 2. PP1 master curve (ref. [1]).

which covered nearly nine decades in time. In addition, the master curve for this particular polypropylene grade exhibited near identical functional behavior with several other PP's to warrant the creation of a general master curve for all polypropylenes (Fig. 3).

When the multiphase polypropylene alloy was subjected to oven aging after irradiation at various temperatures, initial data behaved very normally as in previously studied polypropylenes,

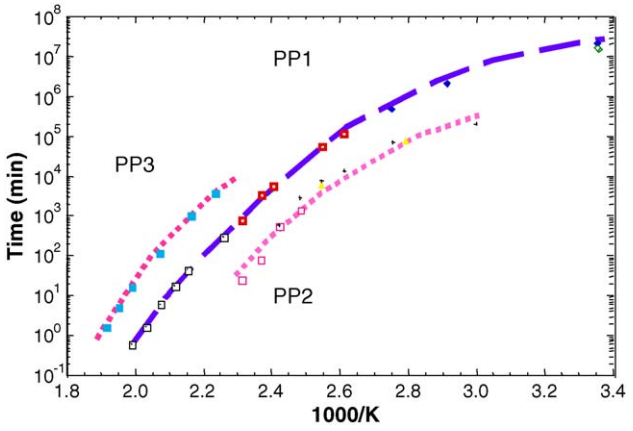

Fig. 3. Master curves for several PP's.

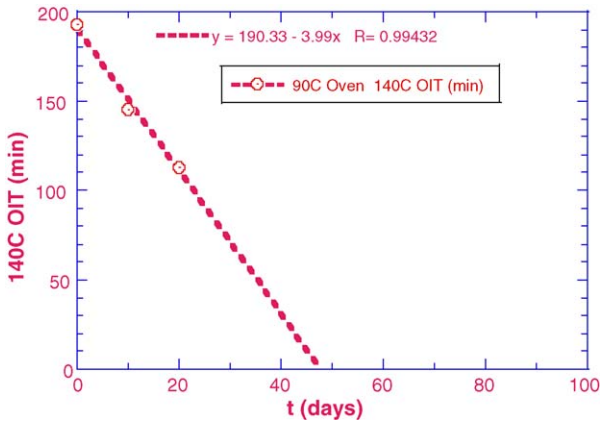

Fig. 4. PP/ULDPE alloy OIT after 90 °C oven aging times.

lending credibility and confidence that the master curve concept may even apply to these alloys. Fig. 4 shows the reduction of of OIT as a function of oven aging time in a 90 °C oven. And extrapolated zero OIT time behavior at 90, 70 and 60 °C oven temperatures was quite linear and well behaved .

However, at the oven aging time of about 30 days, all samples had failed in a brittle fashion while still exhibiting strongly measureable OIT and hence antioxidant contents. Thus, this observation totally invalidated the applicability of master curve through high temperature OIT testing to these multiphase alloys (Fig. 5). Data in this study indicated that very erroneous conclusions could be reached for multiphase alloys if OIT data alone were used toward the master curve construction.

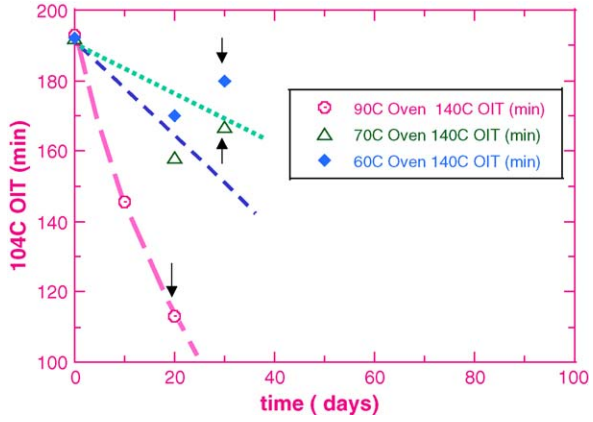

Fig. 5. OIT data, arrows indicate onset of brittle failures.

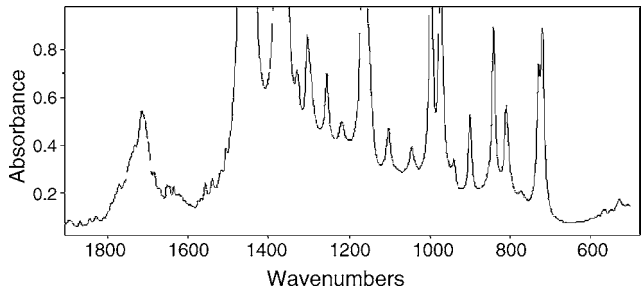

Fig. 6. FTIR of sectioned PP/ULDPE alloy.

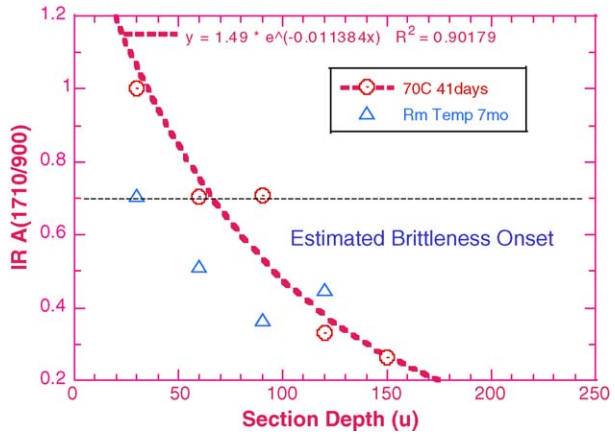

Fig. 7. FTIR of serial sectioned specimens.

Fig. 8. Morphology of cross section.

Further investigation into the failure morphology and FTIR study of serial sectioned depth profiled samples clearly indicated heterogeneous degradation (Figs. 6 and 7). For convenience, the 1710 cm^{-1} band (carbonyl) and the 900 cm^{-1}(polypropylene) band was used for ratio analysis. It is quite evident that the oxygen diffusion limited degradation mechanism first proposed by Gillen and Clough [7] is the governing model for these thick sections with multiple domains. Hence, the finite OIT results measured were from the relatively undegraded interior and polyethylene domains with much greater resistance to degradation. Since PP is very notch sensitive, a degraded and embrittled skin layer constitued sharp notches for crack initation leading to brittle failures. In Fig. 8, a thin (~20 μm) cross section of the alloy was stained with iodine and examined under polarized light. The degraded zone was clearly shown as a dark band on the skin.

4. Summary

Following the procedure established for the oxidative degradation master curve, an injection molded PP/ ULDPE alloy sample was subjected to post irradiation oven aging, and the OIT determined with aging time. However, in sharp contrast with neat polypropylenes, where a master curve behavior was clearly evident, the alloy sample failed in a brittle manner long before the disappearance of measurable OIT or remaining antioxidants. The failure to follow the master curve can be attributed to the heterogeneous nature of degradation both from the surface/bulk differentiation due to oxygen diffusion limited reactions, and the drastically different degradation kinetics and antioxidant consumption between the polypropylene matrix phase and the ULDPE impact modifier domains. Thus, the traditional oven aging OIT master curve approach was found to be unsuited for shelf-life prediction. Any any valid methodology, must properly taking into account the heterogeneous nature of degradation. FTIR methods monitoring the carbonyl concentration in the alloy was found to be quite effective for quantifying the extent of degradation. There is a possibility that the OIT method when used in conjection with FTIR, could create a more general, predictive method for shelf-life prediction for multiphase alloys and heterogeneous degradation pathways. Further experiments in this direction are currently underway.

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