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APPLICATION AND LIMITATIONS ON THERMAL AND SPECTROSCOPIC METHODS FOR SHELF-LIFE PREDICTION

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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 spectroscopic and morphological methods to study the applicability and limitation of these techniques. Results were combined with real life and simulated aging experiments and presented in this article.

***Keywords:** FTIR, multiphase polypropylene, thermal methods*

Introduction

Earlier, we have provisionally established [1, 2] that there is a master curve [3] prescribing the thermal oxidative degradation of polyolefins, especially polypropylene [4, 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 (PP) 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.

Experimental

The polypropylene used was a medical radiation grade random ethylene copolymer with melt flow of 25 dg min^{-1} at 230°C, and the ultra low density polyethylene (ULDPE) had a density of 0.90 g cm^{-3}. Sample of the PP/ULDPE blend in 80/20 mass ratios was injection molded into relatively thick (about 1.2 mm) specimens. Since PP and ULDPE are not thermodynamically miscible, the soft, mostly amorphous ULDPE is expected to exist as isolated domains in the PP matrix phase. 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 various temperatures after irradiation. Samples withdrawn at various time intervals were subjected to the OIT analysis similar to ASTM 3895 [6] in open aluminum pans with the exception of air at flow rate of 100 mL min^{-1} instead of oxygen. For selected samples, a serial sectioning of about 30 micron in thickness was carried out parallel to the sample surface with a Reichert microtome and Fourier Transform Infrared (FTIR) spectra acquired on a Matson FTIR spectrometer fitted with an aperture disk about 7 mm diameter to accommodate the small sample sections. From the FTIR data, the ratio of absorbance peak heights at 1710 (carbonyl) and 900 cm^{-1} (PP) was used to quantify the degree of degradation.

Results and discussion

To better illustrate the master curve concept, data sets from reference [1] used for the master curve construction for PP1 a medical grade polypropylene are presented in Fig. 1. Clearly, the self-similarity of data justi-

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fied the vertical shift procedure for the master curve (Fig. 2) 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, lending credibility and confidence that the master curve concept may even apply to these alloys. Figure 4 shows the reduction 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.

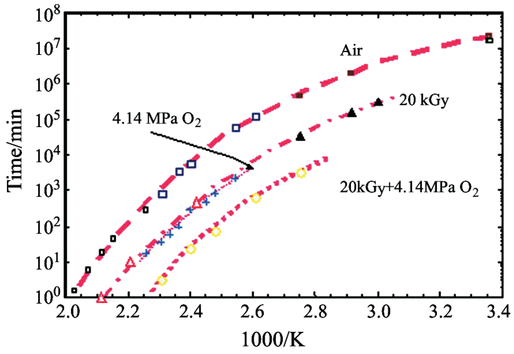

Fig. 1 Master curve construction for PP1 from [1]

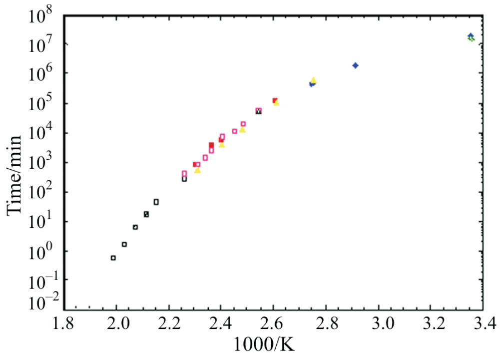

Fig. 2 PP1 master curve [1]

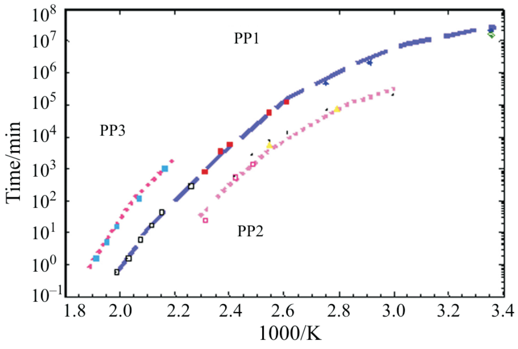

Fig. 3 Master curves for several PP's

However, at the oven aging time of about 30 days, all samples had failed in a brittle fashion while still exhibiting strongly measurable OIT and hence antioxidant contents. These failed samples exhibited very low elongations when subject to a sharp 90° bend. 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. In other words, the master curve describing the antioxidant behavior and the mechanical properties have completely decoupled from each other.

Further investigation into the failure morphology and FTIR study of serial sectioned depth profiled samples clearly indicated heterogeneous degradation (Figs 6, 7). For convenience, the 1710 cm^{-1} band (carbonyl) and the 900 cm^{-1}(polypropylene) band was used for ratio analysis. It was estimated that a ratio of about 0.7 at about 50 micron depth would bring about brittle failures for this sample. 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 un-degraded interior and polyethylene domains with much greater resistance to degradation. Since PP is very notch sensitive, a degraded and embrittled skin layer constituted sharp notches for crack initiation leading to brittle failures. In Fig. 8, a thin (~20 micron) 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.

Conclusions

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

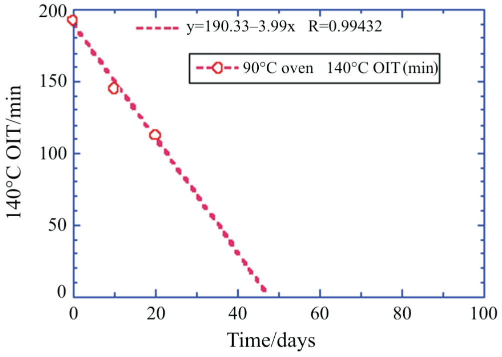

Fig. 4 PP/ULDPE alloy OIT after 90°C oven aging times

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 valid methodology, must properly take 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 conjuction 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.

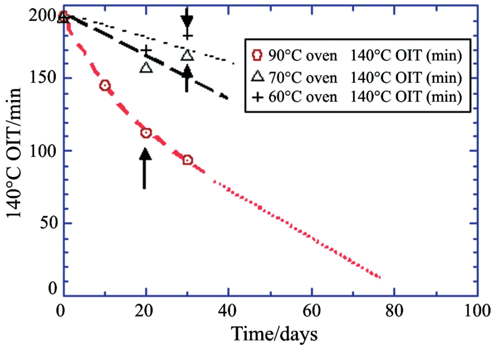

Fig. 5 OIT data, arrows indicate onset of brittle failures

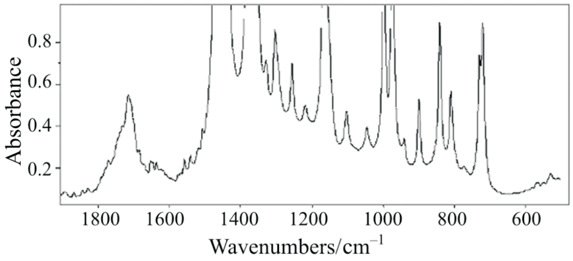

Fig. 6 FTIR of sectioned PP/ULDPE alloy absorbannce *vs.* wavenumbers cm^{-1}

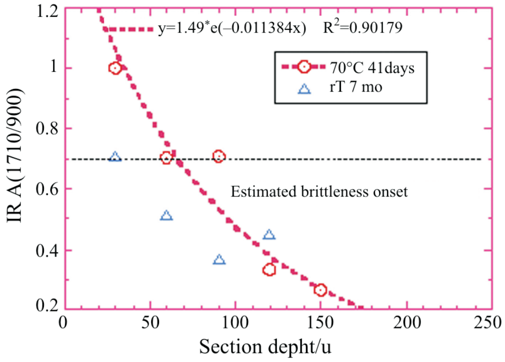

Fig. 7 FTIR of serial sectioned specimens

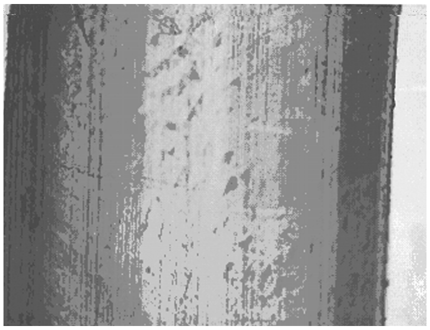

Fig. 8 Morphology of cross section

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