

THERMAL OXIDATIVE STABILITY TESTS, A RE-EXAMINATION

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Abstract

DSC and TGA are two of the most widely used methods for studying thermal oxidative stability of polymers. Previous studies have shown that comparable Oxidative Induction Times (OIT) can be obtained by either method. However, since the two methods measure totally different sample properties during the oxidation process, we conducted a more detailed study beyond the OIT quantity. Polymers which undergo chain scission and crosslinking are compared with both techniques. A further elaboration of a more general kinetics model was also attempted. Result of these evaluations toward assessing the oxidative stability and possible shelf life prediction will be presented

Introduction

Thermal oxidative stability data has often been used to assess shelf life of polymers used in medicine and pharmacy[1-5]. We have previously studied the oxidative induction time (OIT) and its relationship to long-term shelf life of many medical polymers. For example, we found in the thin film form, polyolefins exhibited diminishing activation energy of oxidation as the test temperature was lowered. The OIT measured at high temperatures and oven aging failure times are often presented as a plot of the logarithm of OIT or failure time dependence on the inverse absolute temperature (by analogy with Arrhenius plot). Considering that for polyolefins the extrapolated to zero OIT time (Fig.1) constitutes a conservative estimate of mechanical failures, the resulting master curve enables one to estimate long-term durability [6-11]. To further understand the detailed mechanisms, we re-evaluated and compared OIT from DSC and TGA and analyzed, the physical and chemical significance of the observations.

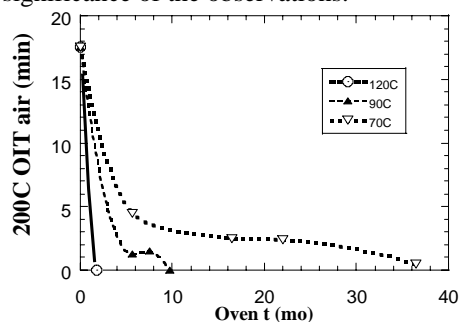


Figure 1, Polyolefin OIT with Long Term Oven Aging

Experimental

A DuPont 910 Differential Scanning Calorimeter (DSC) cell, or a pressure DSC cell, with open aluminum sample pans, and a DuPont 951 thermo-gravimetric analyzer (TGA) controlled by a custom designed controller with LabView® programming were used. And the OIT procedure of ASTM-D 3895 was followed in the main, except air flowing at about 100ml/ min was used instead of oxygen. For the majority of experiments, the isothermal mode was used; the instrument is ramped rapidly to the desired isothermal temperature and t_0 is set at the time of temperature equilibrium. A chain scission random polypropylene co-polymer studied earlier (PP1) of about 2% ethylene, and 1.5 melt flow, and a crosslinking type high density polyethylene (HDPE) ASTM OIT standard (TA Instruments) were used as samples. Both samples were compression molded or extruded to thicknesses of about 0.5mm to minimize diffusion effects.

Results and Discussion

The oxidative degradation reaction is autocatalytic. A radical chain reaction results from a single initiation event (Figure 2) [12, 13]. Thermal oxidation is an exothermic process with the heat evolution delayed by the time corresponding to radical reactions with anti-oxidants (such as hindered phenols). After anti-oxidants molecules are consumed, induction period is over and substantial heat emission is detected.

Following ASTM recommended endpoint selection for the DSC OIT trace, the extrapolated onset is used, where a tangent is drawn at the point of the maximum rate of oxidation and the baseline prior to the oxidation. [5]. Thus, in Figure 3 the measured induction period, or regime I, is defined as the period during which the polymer system is being protected by the sacrificial reaction with anti-oxidants. Thus, without the autocatalytic chain process generating multiple reactions for a single initiating event, the DSC output is constant and close to the instrument baseline. In Regime II, the autocatalytic period, the inhibitor has been totally consumed, and the highly branched chain reaction takes over, a geometric progression of oxidations dominates, with an exothermic event from the DSC. In regime III, the polymer sample is nearly consumed, the heat release from the reacting system diminishes and the DSC signal returns to baseline.

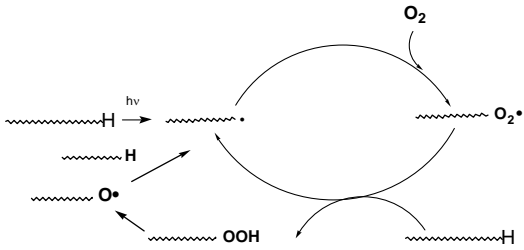


Figure 2, Schematic Oxidative Degradation Pathways

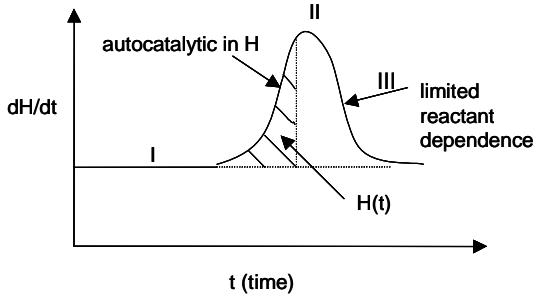


Figure 3, Typical DSC OIT Curve at Different Regimes

For the polypropylene PP1, typical DSC OIT traces are shown in Figures 4-5. The frequently seen multiple onset for data at 180°C is attributed to sample heterogeneity.

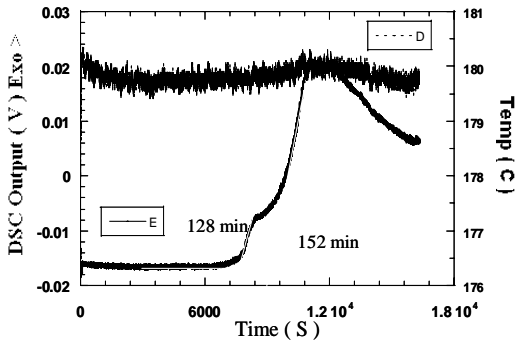


Figure 4, PP1 DSC OIT 180°C

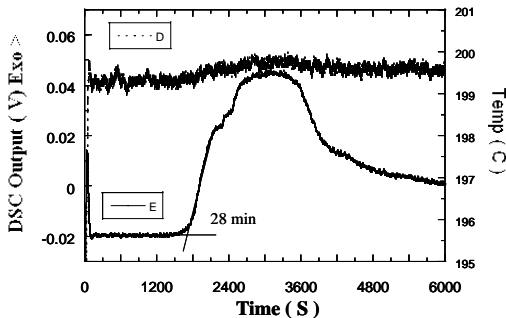


Figure 5, PP1 DSC OIT at 200°C.

The corresponding TGA data at these temperatures are shown in Figures 6 and 7. It is immediately evident that the TGA onset occurred

substantially earlier in the isothermal segment. In addition, there is a steady upward shift of sample mass at both temperatures and became much more pronounced at higher temperatures.

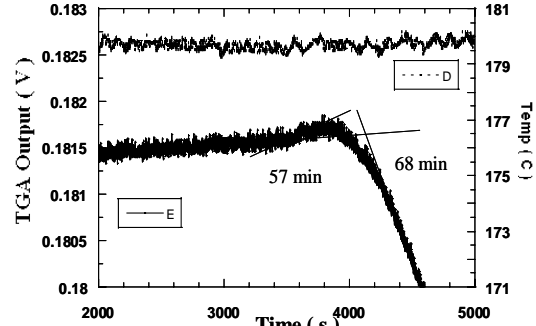


Figure 6, PP1 Oxidation by TGA 180°C

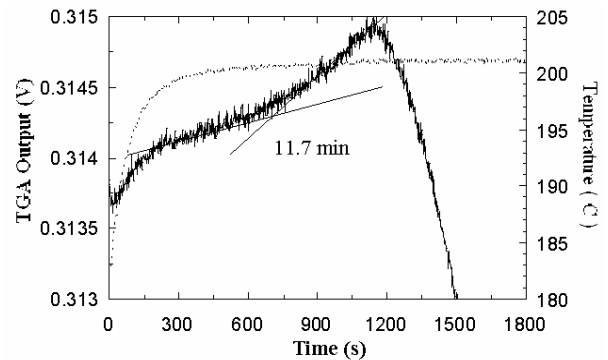


Figure 7, PP1 TGA 200°C

Initial TGA weight gain was also observed in polyethylene samples (Fig. 8). Again, the oxidation induction period monitored by DSC was longer than that obtained by TGA (Fig. 9).

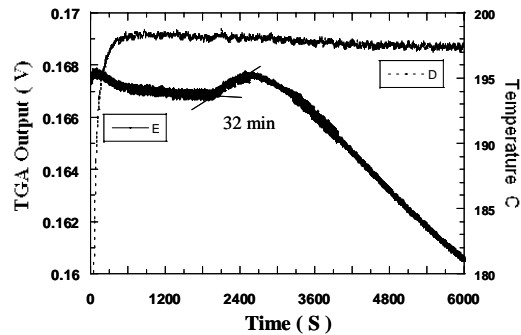


Figure 8. TGA ASTM-D at 200°C.

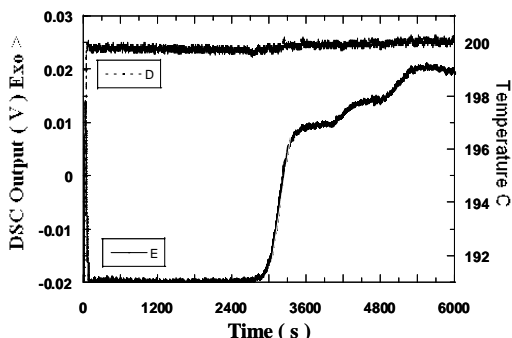


Figure 9, DSC HDPE (ASTM-D) OIT at 200°C

We noted, that the formation of radicals in the absence of oxygen by the reaction



is often endothermic. For example the reaction,



absorbs 372kJ/mol [24]. Even the reactions of radicals with hydrogen donors of the type



is 92kJ/mol endothermic [24].

Peroxide formations are endothermic requiring up to 100kJ/mol to initiate [22-24].



The strong heat release occurs upon chain branching, thus even after antioxidant is nearly exhausted, and the beginning of weight loss detected by TGA, DSC outputs are still negative or negligible.

Although chain process of oxidation is suppressed by antioxidants, incorporation of oxygen still occurs. Thus, the polymer sample gains weight, and TGA trace has an upward slope.

Near the TGA turn over point, where the antioxidant has been consumed and prior to formation of volatile products (such as H₂O and CO₂) leading to weight loss, a chain propagation with formation of large amount of peroxides occurs [12, 13]. This is reflected by a sharp increase in weight seen as a small peak on the TGA curve. Since we noted earlier that peroxide formation is endothermic, the DSC autocatalytic regime is retarded.

To summarize, the weight loss detected by TGA began substantially earlier than the corresponding exothermic effects detected by DSC (Fig. 4-5 vs. Fig. 6-9). This is attributed to the lower or negative enthalpies of earlier events, and much higher enthalpies of later events like radical-radical and oxygen-radical reactions [14- 15].

The late stages of oxidative degradation of polyethylene and polypropylene are rather different (Fig. 10), however, weight increase during the induction period due to reactions with oxygen and DSC-detected induction period longer than detected by TGA are common for both polymers and can be attributed to similar mechanisms.



Figure 10, Crosslinking PE (left) shrinks, PP(right) chain scissions and liquifies.

From a tabulation of the kinetic scheme [13], the time (t) dependence of absorbed oxygen is given in equation 5:

$$[O_2] = \frac{\delta k_p^2 k_d [PH]^2}{2k_t} t^2 \quad (5)$$

where δ is the radical yield per each dissociated hydroperoxide group (2δ is equal to number of kinetic chains generated by each dissociated hydroperoxide). Thus at low degrees of conversion the weight gain due to oxygen absorption should increase parabolically with time ($\propto t^2$), supporting the experimental data observed.

Weight-gain due to oxygen absorption by propylene during 130°C thermal oxidation was monitored and modeled in the past to be as high as 10⁻² moles of O₂ per 1g of polypropylene at 130°C over <120 minutes of exposure [16-25]. These results were also in agreement with absorbed oxygen reaction induced weight gain from the equation above [12, 13]. In a recent report using isothermal TGA method, it was also observed on unstabilized polyolefin samples [26].

Summary

Oxidation induction time (OIT) is widely used to predict the shelf life stability of the polymer in storage and use. We compared two methods of OIT determination, and observed that DSC-monitored oxidation induction time extends substantially past the point when oxidation of polymer and formation of volatile components of polymer degradation is detected by TGA. Endothermicity of the initial stages of thermal oxidation appears to be further responsible for masking the time at which the inhibitor ("antioxidant") is completely consumed and autocatalytic oxidation of polymer itself is initiated. Determination of OIT by TGA is somewhat complicated by the absence of a clear boundary between

the regions of antioxidant dominated induction time and weight gain due peroxides formation on the main chain. It appears, that careful evaluation of the combination of TGA and DSC data on specific polymer system could yield additional insights on shelf-life prediction based on either technique alone.

References

1. N. Billingham, D. C. Bott, and A. S. Manke, in N. Grassie Ed., *Developments in Polymer Degradation-3*, Ch. 3, Applied Sciences Publishers, London, 1981.
2. G. N. Foster, in J. Pospisil, P. Klemchuk eds., *Oxidation Inhibition in Organic Materials*, Vol.2, CRC Press, Boca Raton, 1989.
3. K. Gillen, and R. Clough, in D. W. Clegg and A. A. Collyer Eds., *Irradiation Effects on Polymers*, Elsevier Applied Science, New York, 1991.
4. R. J. Rolando, *J. Plast. Film & Sheeting*, 9(4) (1993) 326
5. *ASTM Standard D-3895-92*.
6. L. Woo, S. Y. Ding, M. T. K. Ling and S. P. Westphal, in M. Keating Ed., *Proceedings of the 11th International Congress on Thermal Analysis and Calorimetry, Vol. I*, John Wiley Ltd., Chichester, 1997, p. 131-138.
7. L. Woo, M. T. K. Ling, A. R. Khare and S. Y. Ding, in L. Mallinson, Ed., *Ageing Studies and Lifetime Extension of Materials*, Kluwer Academic/Plenum Publ., New York, 2001, p. 499-506.
8. L. Woo, S. Y. Ding, M. T. K. Ling, and S. P. Westphal, in A. T. Riga and G. H. Patterson, Eds., *Oxidative Behavior of Materials by Thermal Analytical Techniques*, ASTM STP 1326; Am. Soc. of Testing Materials, Philadelphia, 1997 p. 44-57.
9. L. Woo, A. Khare, H. P. Blom, C. Sandford, S. Y. Ding, *Therm. ACTA*, p367-368 (2001) 113.
10. R. L. Blaine and M.B. Harris, in A. T. Riga and G. H. Patterson, Eds., *Oxidative Behavior of Materials by Thermal Analytical Techniques*, ASTM STP 1326, Am. Soc. of Testing Materials, Philadelphia, 1997, p.193-204. .
11. B. Eu, C. Sandford, M. T.K. Ling, and L. Woo, *Proc. North American Thermal Analysis Soc. Conf.*, 2004.
12. N. M. Emanuel, A. L. Buchachenko, *Chemical Physics of Polymer Degradation and Stabilization*, New Concepts in Polymer Science Series, VNU Science Press, Utrecht, Netherlands, 1987.
13. A. S. Kuz'minskii, B. N. Leyland, Eds., *The Ageing and Stabilization of Polymers*, Elsevier, Amsterdam, London, New York, 1971.
14. S. W. Benson, *Thermochemical Kinetics. Methods for Estimation of Thermochemical Data and Rate Parameters*, McGraw-Hill, New York, 1968.
15. V. V. Krongauz, C. P. Chawla, *RadTech Report*, Sept./Oct. (2001) 34
16. J. Crank, G.. S. Park, Eds., *Diffusion in Polymers*, Academic Press, New York, 1968
17. W. J. Koros, Edtr, *Barrier Polymers and Structures*, ACS Series, ACS, Washington, DC, 1990
18. V. V. Krongauz, E. R. Schmelzer, *Polymer*, 33(9) (1991) 1893.
19. V. V. Krongauz, E. R. Schmelzer, *Proc. SPIE, Photopolymer Device Physics, Chemistry, Appl.*, San Diego, CA, 1559 (1991) 354.
20. V. V. Krongauz, E. R. Schmelzer, R. M. Yohannan, *Polymer*, 32(9) (1991) 1654
21. V. V. Krongauz, *Diffusion in Polymer Matrix and Anisotropic Photopolymerization*, in V. V. Krongauz, A. D. Trifunac Eds., *Processes in Photoactive Polymers*, Chapman & Hall, New York, Toronto, etc., 1995.
22. S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill Book Co., New York, 1960.
23. Kh. S. Bagdasar'yan, *Theory of Free-Radical Polymerization*, Israel Program for Scientific Transl., Jerusalem, 1968.
24. D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, Th. Just, J. A. Kerr. M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker, J. Warnatz, *J. Phys. Chem. Ref. Data*, 34(3) (2005) 757.
25. R. Kumar, G. Madras, *J. . Appl. Pol. Sci.*, 90 (2003) 2206.
26. A. A. Calhoun, *Proceedings SPE ANTEC*, (2007) 531.

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