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Applications of the oxidative induction test to medical polymers [α]

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Abstract

We have examined the applicability of this simple and effective test to polymer systems widely used in the medical industry. First, it was found that not every polymer examined exhibited a distinct onset of autocatalytic oxidation detectable by DSC. However, for cases where distinct onsets are found, powerful insights can be obtained. These included the activation energy of the degradation, thermal oxidative shelf life prediction, and correlation with product performance. Actual examples will be presented to illustrate the utility of the test.

INTRODUCTION

The oxidative induction test (OIT) is one of the most powerful and practical methods frequently employed to obtain information on base polymer stability, antioxidant additive effectiveness, and the relative degree of degradation during processing [1–5]. The test was originally developed at the Bell Telephone Laboratories for the study of polyolefin insulation material stabilities, and subsequently adopted by ASTM as a standard test method [6]. We found it particularly useful in aiding the development of a stabilizer system for medical plastics. Polymer materials such as polyvinyl chloride (PVC) and vinylidene chloride copolymers (PVDC) are well known to undergo thermal dehydrochlorination degradation during product fabrication, and stabilizers are needed to insure good product performance. For example, it was found during this study that, in the PVC system, the thermal stability as a function of one of the stabilizers actually goes through a maximum. After the optimum concentration is passed, the polymer system suffers a reduction in stability as the stabilizer concentration is increased. Thus, for PVC and other polymers, an oxidative induction test can be applied to quantify the effectiveness of the stabilization system in a convenient, simple, rapid, and cost effective manner.

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In the OIT test, if a distinct onset can be determined, it is a unique determination of the total stability of the sample examined. Contributing to this total stability are the intrinsic and extrinsic factors relating to the sample at hand. Examples of the intrinsic factors are: polymer type (e.g. polyethylene vs. polypropylene with tertiary pendant groups), molecular weight (number and stability of chain ends), main chain imperfections and their instability (e.g., head to tail sequences, residual unsaturation and branch points), etc. Post-polymerization and the selection and method of incorporation of the stabilizer package are critically important. Subsequent to manufacture, numerous converting operations all have an impact on the stability of the final products. Processing histories, including temperature, shear rate, residence times and radiation sterilization are some of the commonly encountered variables. And finally, shipping, distribution, and shelf life under various time, temperature and humidity conditions and visible/UV light exposures constitute the extrinsic controlling factors.

In this study, we will investigate the applicability of the OIT method to olefinic, acrylic and halogenated materials. We will also examine the effect of molecular weight, concentration and type of stabilizers on the stability. Finally, an attempt is also made to relate product performance with the measured oxidative induction time.

EXPERIMENTAL

The oxidative induction test was conducted on a Du Pont 1090 thermal analyzer with a 910 differential scanning calorimetry (DSC) cell. Normally this test has two modes of measurement, that is, oxidative induction temperature and oxidative induction time. Oxidative induction temperature indicates the onset of auto-oxidative reaction while the temperature is scanned at a preset rate. For this mode of testing, usually a thin and flat specimen, typically about 2 mg or less, was prepared and placed in an open aluminum sample pan and secured on the thermoelectric disk of the DSC cell. The sample was then scanned at a rate of $20\,^{\circ}\mathrm{C\ min}^{-1}$ from ambient to 300°C or higher in an air purging stream of $100\ \mathrm{ml\ min}^{-1}$. The second mode, the oxidative induction time, provides a relative measure of the degree or level of stabilization of the material tested. Specimen preparation is the same as in the continuous temperature scanning method, except for scanning in a nitrogen gas environment to the preset isothermal testing temperature. Once temperature equilibrium has been established, the controller automatically switches purge gas to air or oxygen at the same purging rate. The changeover point to air or oxygen purge is taken as the zero time of the experiment. The oxidative induction stability of the test samples is assessed by monitoring an abrupt exotherm or endotherm departure from the baseline, as indicated by Fig. 1 [7]. Often, if the reaction follows simple zero order kinetics, induction time measured at various temperatures can be used to construct an Arrhenius

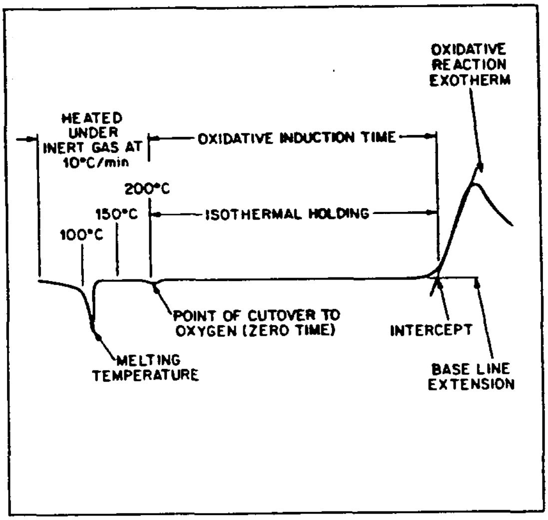


Fig. 1. Oxidative induction time scan of polyethylene [6].

plot, expressed as log(OIT^{-1}) versus T^{-1}, to obtain information on the oxidation reaction kinetics. Mathematically, the rate constant K, which is proportional to OIT^{-1}, may be expressed in the Arrhenius form as

$$K = K_0\ e^{(-\Delta E/RT)} \tag{1}$$

where K_0 is the pre-exponential factor, ΔE is the activation energy of the reaction, R is the gas constant, and T is the absolute temperature in Kelvin. The slope of the log K vs. T^{-1} plot is then the activation energy divided by R.

Specimens less than 100 μm in thickness were used throughout this study to ensure homogeneity. Inhomogeneity could result in multiple oxidative transitions, as indicated in Fig. 2; therefore, in normal cases, it should be avoided. Inhomogeneity usually arises from the skin and core of molded

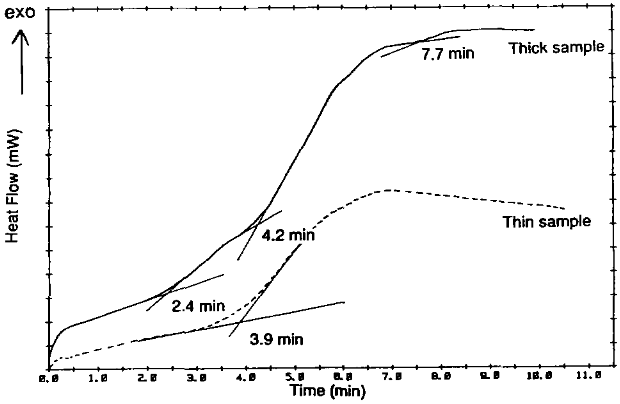


Fig. 2. OIT of polypropylene at 220°C, thick and thin sample.

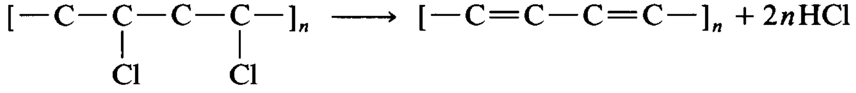
sections, spatial variations in composition or thermal histories. With thin sections and small sample sizes, all of the inhomogeneities are likely to be resolved, and differentiation of skin and core thermal and aging histories is made possible and meaningful.

Materials included in this study were polyvinyl chloride (PVC) with different molecular weights and various plasticizer contents; polypropylene (PP), ethylene vinyl acetate (EVA) with different amounts of antioxidants, and polymethyl methacrylate (PMMA). Also, high density polyethylene (HDPE) with different levels of antioxidants was examined.

RESULTS AND DISCUSSION

To check the applicability of the test to a wide variety of polymer systems, we conducted trials over broad ranges of temperature and time conditions. It was found that not every polymer gave distinct, easily definable onsets, especially during isothermal time scans with air or oxygen flowing over the sample in an open pan. PVC, as suspension polymerized granules, failed to give distinct onsets, while compounds with calcium zinc stearate primary stabilizer and epoxidized oil secondary plasticizer gave extremely sharp, well defined and reproducible results. In general, for polymethyl methacrylate (PMMA) and related polymers, where the degradation mechanism is primarily via chain unzipping and monomer evolution, no distinct onsets were detected with our current procedures. For most of the polyolefins and many elastomer systems, good, distinct onsets were easily detectable. Our experience has shown that, with manipulation of experimental conditions such as sample size, heating rate, and isothermal temperatures, easily definable onsets can be obtained for the great majority of materials.

We also recognized that, for the most part, the action of the stabilizers is nearly always sacrificial, that is, they react preferentially with the challenging media such as active oxygen, propagating free radical species, etc. When the stabilizer is totally consumed, then the degradation reaction should proceed at a much accelerated rate, giving a detectable DSC output. The classical oxygen uptake experiment for determining stabilizer effectiveness is based on this occurrence. Also, many of the polymer degradation products are potent catalysts for further degradation reactions. A well known example is the dehydrochlorination reaction of PVC



$$[-C-\underset{\substack{|\\ \mathrm{Cl}}}{C}-C-\underset{\substack{|\\ \mathrm{Cl}}}{C}-]_n \longrightarrow [-C=C-C=C-]_n + 2n\mathrm{HCl} \qquad (2)$$

Once liberated from the main chain, the hydrogen chloride catalyzes further electrophilic reactions that eliminate more HCl. In this way, an abrupt, endothermic event corresponding to the resulting polyene formation

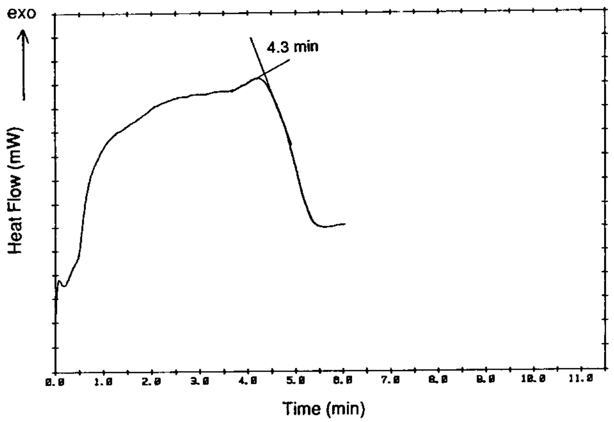


Fig. 3. A typical OIT of PVC.

is detected, giving insight into the mechanisms of degradation. We also noted with interest that this particular reaction is endothermic, in contrast to most thermal oxidative reactions. Since the dehydrochlorination reaction is the reverse of an addition reaction to the double bond, heat absorption takes place to create the conjugated polyene sequences. Figure 3 is a typical PVC OIT thermogram. Experiments on the additivity of the OIT reaction indicated that for this system, the measured OIT is additive. In other words, the degradation reaction kinetics are zero order to a very good approximation. Thus the inverse of the oxidative onset time would be proportional to the rate constant. Activation energy of dehydrochlorination of ≈ 37 kcal mol^{-1} was calculated from the slope of OIT^{-1} versus T^{-1}, Fig. 4. The measured activation energy falls in the typical range for degradation reactions.

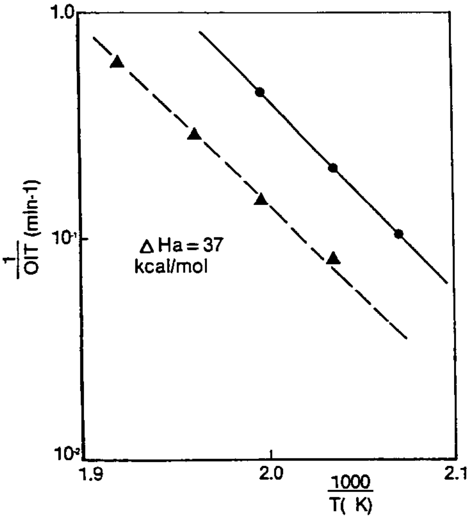


Fig. 4. PVC formulations: oxidation kinetics.

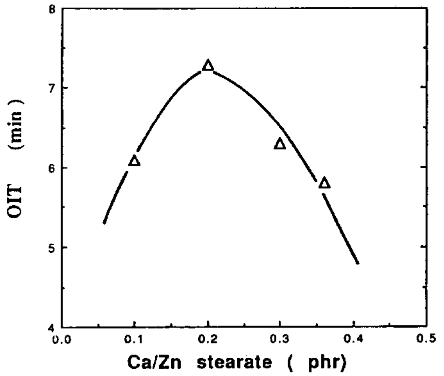


Fig. 5. PVC formulation stability.

In another series of studies, the dependence of PVC thermal stabilities measured as OIT was determined while the concentration of stabilizer was systematically varied. It was found that a rather sharp maximum existed with regard to the concentration of the primary stabilizer, a calcium zinc stearate at ≈ 0.2 phr or ≈ 0.13%, for the system studied, while an extremely linear relationship was found for the secondary stabilizer, in this case an epoxidized oil (Figs. 5 and 6). In summary, the PVC stability function spanned a three-dimensional design space as schematically depicted in Fig. 7. The utility of graphs such as Fig. 7 in polymer stabilization system development is readily apparent.

In a separate set of experiments, the stability of PVC resins of different molecular weights was compared by means of their OIT behavior. In general, it is anticipated that increasing the molecular weight of the polymer should increase the oxidation resistance owing to the lower concentration of less stable and more reactive chains ends [8], but we have found a reversal of this trend when the molecular weight reaches 10^5 as shown in Fig. 8. This apparent reversal is possibly because the chain ends had been stabilized by chain transfer agents in the termination process during polymerization. In

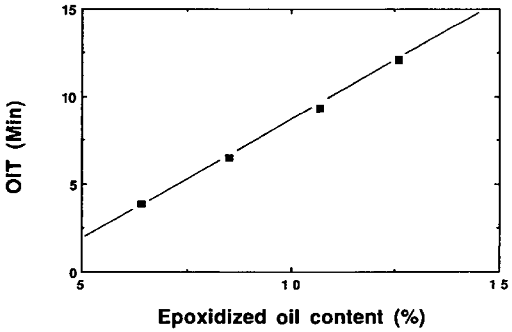


Fig. 6. PVC: oxidative stability vs. epoxidized oil content.

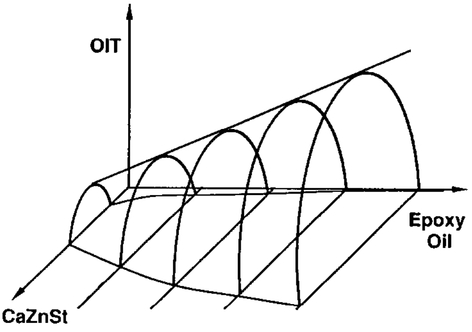


Fig. 7. Schematic stability surface for PVC formulations.

other words, the high molecular weight product has a smaller number of less stable chain ends, and the overall stability is decreased. In this way, by using identical formulations, intrinsic stabilities of resins of different sources and manufacturing conditions can be readily compared.

One of our polypropylene component products encountered failures due mainly to material degradation. This is evidenced by comparing an oxidative induction time of 3.2 min for failed components versus 11 min for intact components. Not only is the oxidative induction test an excellent method for trouble shooting but it can also be used for the determination of optimal time and temperature during extrusion or molding. We have also conducted an experiment to check the additivity of degradation for PP at 210°C. Samples were heated in a nitrogen gas environment to 210°C and held isothermally for 2, 3 and 5 min in air, then rapidly cooled to ambient temperature and again reheated to 210°C, and the oxidative induction times were then recorded. There is no doubt that the degradation follows the law of addition, as demonstrated in Fig. 9. This is the second polymer system where the apparent kinetics of the degradation reaction followed a zero order reaction. Activation energy of PP degradation was measured to be 36 kcal mol^{-1}, see Fig. 10.

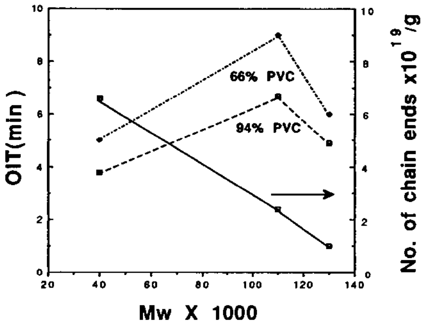


Fig. 8. Stability of PVC formulations as a function of molecular weight and chain ends.

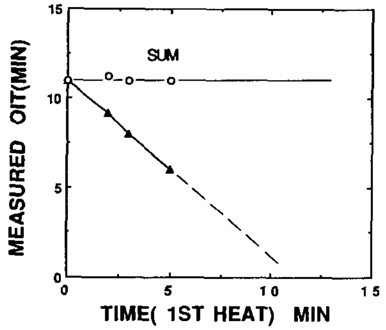


Fig. 9. Additive behavior of OIT of polypropylene at 210 ° C.

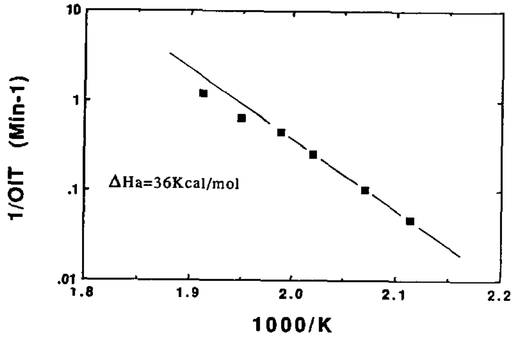


Fig. 10. Polypropylene: oxidation kinetics.

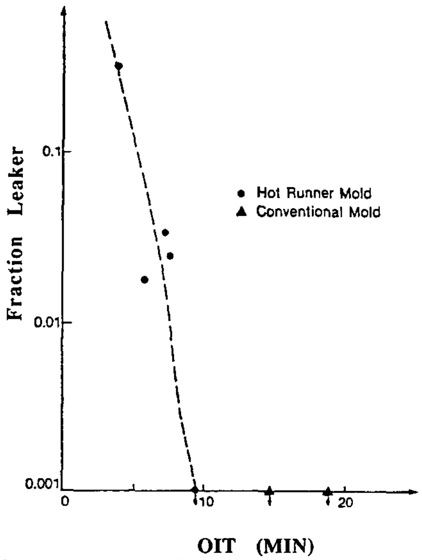


Fig. 11. Heat seal performance vs. OIT.

Another application of the oxidative induction test was the correlation of product performance in terms of heat seal integrity, as shown in Fig. 11. In a comparison of the conventional mold and hot runner mold produced components, the former displayed much less degradation and heat seal leakage. Evidently, extended residence times in the hot runner system led to significant degradation of the material which in turn affected the surface and rheological properties, which are important in the heat seal performance. In addition to vividly portraying the dependence of performance on processing parameters, the minimum oxidative induction time was also established for the purpose of quality control. For example, a minimum of a 10 min oxidative induction time will insure a product failure rate of less than one in a thousand, or 0.1%.

Another system studied was ethylene vinyl acetate copolymer (EVA) with about 28% vinyl acetate content to verify the effect of Irganox 1076 at 500 ppm and 1000 ppm concentrations. The two formulations were found to have oxidative induction temperatures of 217 °C and 220 °C, respectively. Evidently, increases in oxidative induction temperature arise from the increased protection from the additional antioxidant. However, it is not doubled, as was concentration!

In yet another study, we compared OIT results on HDPE with real-time stability results available in the literature. Klemchuk and Horng [9] conducted extensive long term stability studies on HDPE with either zero (unstabilized) or 0.1% of Irganox 1010. Oxygen uptake and mechanical property data of up to several years were determined. To generate a nearly equivalent sample as in their study, HDPE pellets of density about 0.96 were first exhaustively extracted with methylene chloride to remove all antioxidants, dried thoroughly in an vacuum oven, and melt compounded with 0.1% of Irganox 1010 in a Brabender mixer. The measured OIT values at much higher temperatures in this study are plotted in Fig. 12 with data from oxygen uptake induction times from the Klemchuk study. Surprisingly, both sets of data were found to fall on the same extrapolated line, indicating

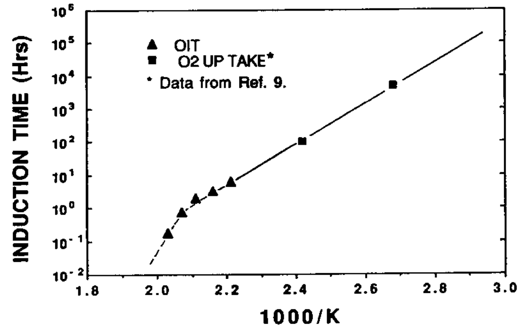


Fig. 12. Arrhenius plot of high density polyethylene with 0.1% of Irganox 1010.

nearly identical reaction kinetics and mechanisms. Furthermore, since Klemchuk et al. have determined the mechanical properties as a function of oxygen uptake, this allowed us to cross correlate mechanical properties from the OIT, to give a reasonable estimate of actual service life at lower temperatures. Of course, the usual precautions must be applied in these kinds of property estimates [4,10,11].

CONCLUSIONS

The oxidative induction test method was applied to a wide variety of polymers to check its applicability. We have been very successful in using this method for the determination of activation energy of oxidative degradation, antioxidant effects, optimal processing parameters, and correlation of product performance if oxidation is the primary governing parameter. It was found that neat PVC and PMMA did not give distinct onsets of oxidation, but plasticized and stabilized PVC compounds give a well defined and reproducible OIT onset. Degradation mechanism of PMMA is primarily through main chain unzipping and monomer evolution, resulting in no distinct OIT onsets detected under our current procedures. The measured activation energy for plasticized PVC compounds and polypropylene were 37 kcal mol^{-1} and 36 kcal mol^{-1}, respectively. The close agreement between these two activation energies for degradation is most probably due to the common feature of the presence of the tertiary group.

In addition, the OIT was found to be additive for several of the polymer systems studied, implying a zero order kinetic phenomenon, allowing a determination of the activation energy of the reaction. In conjunction with the activation energy, one can determine accurately the stability of a polymer or fabricated articles at any temperature. From the examples presented in the text, OIT was found to be a most potent method that relates to and controls product functionality.

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