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STUDY ON THE OXIDATIVE INDUCTION TEST APPLIED TO MEDICAL POLYMERS

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Abstract

This article continues our study published earlier on the application of the oxidative induction test to a wide variety of medical polymers.

In a series of thermoplastic olefin elastomers (TPO), the extrapolated induction time on the Arrhenius plot was found to coincide with published results based on oven aging mechanical studies extending to much lower temperatures and times as long as nearly a year. This agreement indicates the potential of the OIT for long term durability prediction.

For medical flexible PVC compounds, the traditional measure of extent of degradation by color formation was found to correlate to measured oxidative induction times. Furthermore, three distinct regimes were also detected, where in the first phase, little color changes can be detected.

In a longer time, lower temperature study, effect of room temperature fluctuations was clearly detected, emphasizing the need for good environmental control for sensitive detections. These and other recent results will be presented to illustrate the utility of this versatile test.

Keywords: durability, medical PVC, OIT, oxidative stability

Introduction

We have previously studied the utility of the oxidative induction test applied to many of the medical polymers [1]. It was found that in numerous cases, if a clear induction point can be found, important insights can be generated on polymer stability, antioxidant formulation effectiveness, and product and process performances. In this study, we will continue by examining several systems in further detail in the hopes of gaining additional information about optimizing the product or process.

Experimental

ASTM Procedure D3895-80 was followed in the main, except air is used instead pure oxygen, and both the isothermal oxidative induction time (OIT) and temperature scanning induction temperature were used.

The oxidative induction test was conducted on a DuPont 1090 thermal analyzer with 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 measures the onset of auto-oxidative

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reaction while the temperature is scanning 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°C min^{-1} from ambient to 300°C or higher in an air purging stream of 100 ml min^{-1}. The second method, the oxidative induction time, is a relative measure of the degree or level of stabilization of the material tested. The 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 tested 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 a simple zero order kinetics, induction time measured at various temperatures can be used to construct an Arrhenius plot, expressed as log (OIT^{-1}) *vs.* 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:

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

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

Specimens less than 100 microns in thickness were used through out this study to ensure homogenization. Inhomogeneity could result in multiple transitions, and should be avoided. Inhomogeneity usually arises from skin and core of molded sections, spatial variations in composition or thermal histories. With thin sections and small samples, all inhomogeneities are likely to be resolved, and differentiation of skin and core, thermal histories made possible and meaningful.

Results and discussion

Sensitivity considerations

Most OIT experiments are conducted at temperatures around 200°C. If the temperature were much higher, undesirable side reactions and concerns over realistic simulation over near ambient conditions could arise. For example, it is well known many of the commonly used antioxidants begin to volatilize at these high temperatures. As a result, the apparent stability under these conditions are underestimated.

To accurately simulate near ambient durability situations, it is desirable to conduct the experiment at the lowest temperature possible. However, as test temperature decreases, the energetics of the oxidative reaction also diminishes, placing a greater demand on detection sensitivity and noise stability of the instrument. A frequently overlooked parameter is the environment stability over longer experiment

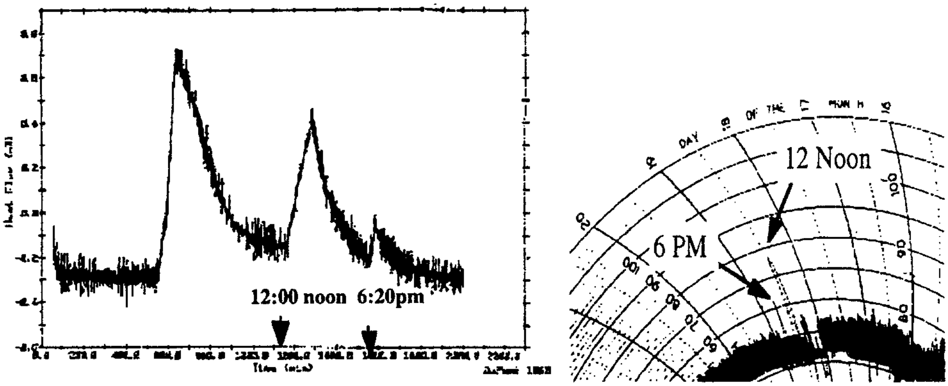


Fig. 1 Anomalous thermal events and room temperature record

times. Figure 1 depicts the instrument output of an actual isothermal experiment at 160°C. The induction time onset is clearly visible as the first transition. However, there were also two distinct "apparent" exothermic events with somewhat different lineshapes. An investigation into the source of the spurious exotherms uncovered two laboratory temperature upset events coinciding with the DSC output. From the laboratory temperature recording chart for the ASTM condition facility set at 22°C, a peak swing to almost 31°C was registered. The sizable detected output serves to emphasize the importance of minimizing room temperature and line voltage fluctuations for the optimum detection of subtle thermal events at lower temperatures.

Olefinic thermoplastic elastomers

A new class of thermoplastic elastomers was created when olefinic polymers (polyethylene, polypropylene) are dynamically vulcanized with a crosslinkable elastomer such as ethylene propylene diene rubber (EPDM). These so-called thermoplastic vulcanizates (TPV) are quite resistant to oxidation and studies have been available on their stability over long times [2]. A general purpose thermoplastic sample of 50 Shore D hardness from the same manufacturer was chosen for the OIT study. Published data from a long-term oven aging study for 50% strength reduction was plotted on the same graph for comparison (Fig. 2).

It is quite evident, that the high temperature OIT accurately predicted long-term oven aging strength retention. It is also noted that the combined data exhibits a slight sigmoidal shape at both temperature extremes, indicating there may be other reaction mechanisms beginning to assert effects on a very broad linear regime covering almost 6 decades of time.

PVC formulations

Polyvinyl chloride is a unique polymer providing wide property spans in the medical field by simply adjusting the level of plasticizers in the formulation. In selecting different base polymers, the intrinsic stability of the neat polymer is an im-

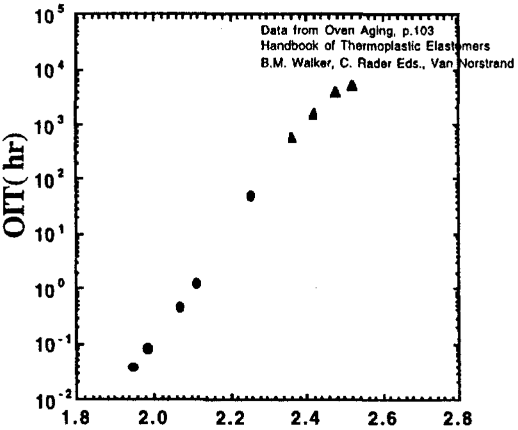
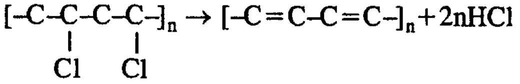


Fig. 2 Olefinic TPV OIT durability comparison

portant consideration. The intrinsic stability arises from the perfection of the polymer main-chain, head to head additions, degree of unsaturation and is mainly a function of the polymerization process conditions during manufacturing. Since chain imperfections will lead to degradation tendencies and the formation of extractible impurities it is important to minimize them.

The degradation of the PVC is primarily a cationic dehydro-chlorination chain reaction [Eq. 2], and most stabilizing schemes are directed toward the elimination of labile reaction sites and the sequestration of the hydrogen chloride as soon as it is produced to avoid further catalyzing neighboring groups.


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

In a study comparing suspension PVC resins from different suppliers. We noted that based on various factors, for example, polymerization temperature, size of the reactor and agitation, type of initiator and suspension agents, and degree of conversion and whether chain transfer agents are used to control molecular weight, various chain ends and chain imperfections were created. These factors should lead to measurable differences in the induction times.

However, neat PVC resins in the form of suspension powders do not give a distinct onset. Thus, a semi-micro scale solution blending method was devised to generate PVC compounds for analysis. The OIT data at 230°C are shown in Fig. 3 with the standard deviation shown as error bars.

Figure 3 also compares the formulation stability from resin supplier A prepared by two methods, the semimicro laboratory method and a large scale extruded film. The slightly extended induction time from the laboratory sample clearly indicated the less severe thermal and shear history of the solution blends compared with melt extrusion. However, the significantly larger standard deviation also reflected less

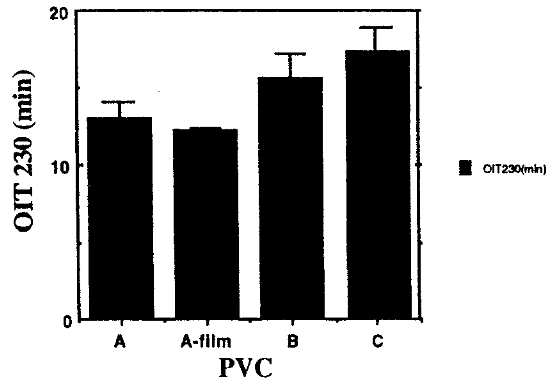
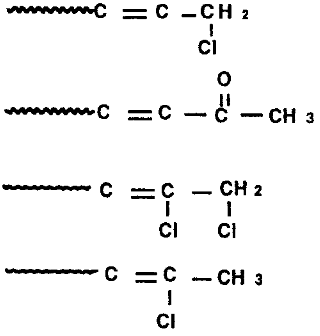


Fig. 3 PVC resin stability



$$\sim\sim C{=}C{-}CH_2Cl$$
$$\sim\sim C{=}C{-}C({=}O){-}CH_3$$
$$\sim\sim C{=}C(Cl){-}CH_2Cl$$
$$\sim\sim C{=}C(Cl){-}CH_3$$

Fig. 4 Suspension PVC chain ends, from ref. [3]

homogeneity. In a similar way, one can state that resins from suppliers B and C are significantly more stable inherently without going through a large scale compounding and extrusion step.

Literature indicated various unstable chain ends (Fig. 4) in suspension polymerized PVC [3]. In a series where suspension PVC powder from the same manufacturer with different molecular weights were similarly compared for their inherent stability, and their OIT at 230°C plotted against the molecular weight, or the number of chain ends per unit volume.

When the results in Fig. 5 were examined, it was noticed that the sample at about 110 K dalton Mw exhibited an anomalously high stability as the one would expect from the concentration imperfections form chain ends. However, an inquiry into the PVC manufacturing process revealed that for this polymer, the molecular weight was controlled by the addition of a chain transfer agent. Since the chain transfer agent would invariably "cap" the reactive chain-ends, enhanced inherent stability was achieved. This example clearly revealed that when a series of polymers of similar compositions were compared under identical conditions, very subtle, often chemically difficult to determine structural differences can be obtained by OIT.

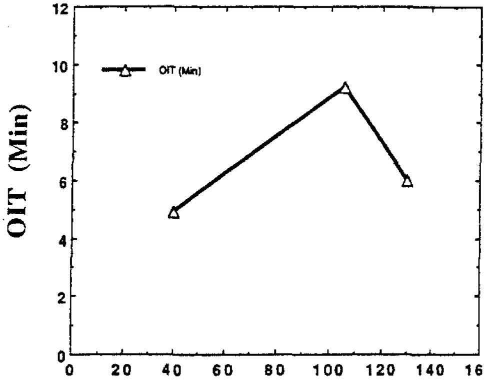


Fig. 5 Supplier A PVC OIT *vs.* Mw

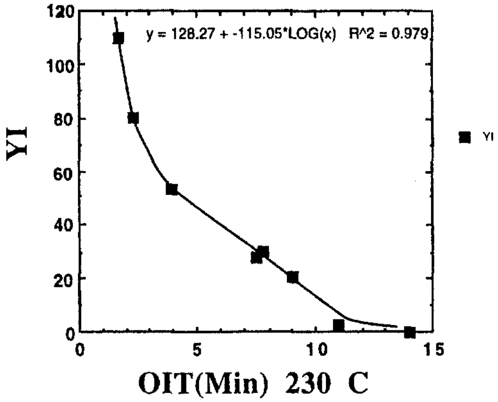


Fig. 6 PVC OIT, COLOR correlation

In another series, PVC films subjected to a standard heat aging test were used. In the heat aging test, film samples were conditioned in a circulating hot air oven at 190°C for various times and the resultant color formation as an indication of relative processing stability. In this case ASTM test of yellowness index [4] was used as the determination of color. The basis of color came from the cationic dehydrogenation degradation mechanism for PVC. As hydrogen chloride is liberated from the PVC matrix, it coordinates onto a neighboring tertiary carbon (most reactive), forming a very stable allylic carbonium ion, before eliminating another HCl molecule to propagate the reaction [5]. In so doing, a series of conjugated dienes (polyenes) were formed. Since the π electrons on these conjugated dienes can freely move over the entire length of the conjugated diene, a one-dimensional electron well resulted. As the diene increases in length, the energy levels and the absorption spectra of the free electron begin to move from UV toward the visible wavelengths. As the absorption spectra increase in intensity from the shortwave length direction, the originally clear PVC film starts to appear yellow to dark yellow, orange, red, and finally black as the degradation progresses.

When the yellowness index of these films were compared with OIT measured at 230°C, a very good correspondence was obtained (Fig. 6).

Not only one can uniquely determine the degree of the degradation compared to the color formation as evidenced by the fit of the data, subtle indications arising form the mechanisms of the degradation are also evident. Figure 6 clearly indicates that the degradation of the PVC proceeds in three distinct phases. In the initial phase, significant induction time were lost without detectable color formation. The second phase indicated a more or less linear dependence of OIT with color. And the final phase, as the stabilizer becoming exhausted and numerous poly-ene sequences simultaneously moving in from the ultraviolet, the color formation becomes exponential before total destruction. The first and initial phase deserves further comment. If, in the absence of significant and detectable color, extensive degradation reaction can take place as measured by OIT, the consequence on chemical extractable must be extensive. This may offer a rapid and effective screening method on chemical and leachable testing.

Polyester elastomer

Polyester thermoplastic elastomers (TPE) based on polybutylene terephthalate (PBT) hard segment and tetramethylene ether (PTMO) soft segments constitute an important class of medical elastomers [6] because of their wide property range, solvent bonding capability, oxidative stability and processing ease. In a series of experiments film samples of 40 D hardness were prepared on a 38 mm laboratory extruder at similar processing conditions but at varying thicknesses. Figure 7 presents the OIT activation enthalpy plot of two of the films. Both the 100 micron (4 mils) and 200 micron (8 mils) film exhibited identical activation enthalpies, indicative of identical oxidation chemistry. A two-layer composite of the thinner film also exhibited identical OIT of the thinner film. This indicates that the sample thickness of the OIT sample is not a primary variable for the induction times measured. However, between the two sets of data, there was about a three-fold difference. An inquiry into the details of the film extrusion process revealed that the thinner film was processed at slightly higher temperatures (193°C *vs.* 176°C). However, temperature

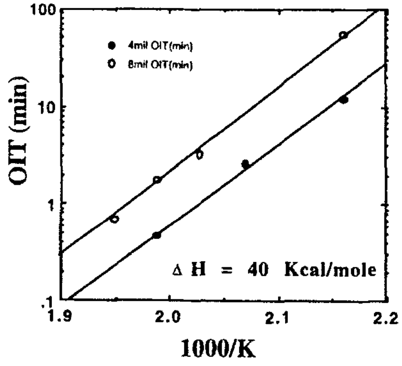


Fig. 7 Polyester TPE processing

alone could not account for the magnitude of the observed OIT discrepancy. It was concluded that the residence time in processing the thinner film must have been significantly longer than the 200 micron film. In other words, Fig. 7 maps out a time temperature envelop for processing this particular polymer without significantly depleting the antioxidant package.

Conclusions

This continuation of the earlier study further illustrated the power and utility of the oxidative induction test applied to medical polymers. To achieve better correlation with ambient temperature durability, lower experimental temperatures could be used, although strict attention must be pay to control ambient environmental conditions. For a family of olefinic thermoplastic elastomers (TPO), OIT data fitted well with published durability data extending to nearly a year: confirming the utility for shelf life screening. Likewise, PVC resin inherent stability and compound heat stability were established.

In addition, the OIT data's ability to assess processing history was confirmed in a polyester elastomer series, further demonstrating the utility for process and product optimization.

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