

MEASUREMENT OF THE OXIDATIVE STABILITY OF POLYETHYLENE BY DIFFERENTIAL THERMAL ANALYSIS

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An evaluation has been made of the experimental features critical to the evaluation of the oxidative stability of polyethylene using constant temperature DTA, with particular reference to the control and measurement of the sample temperature.

The use of the DTA technique at constant temperature to measure the oxidative stability of polyethylene and other polyolefines as an alternative to the oxygen adsorption method is well established [1, 2]. However, the DTA method relies heavily on the rigorous control of experimental factors in order to produce reliable and accurate results. One main method for the measurement of oxidative stability involves heating the test sample at a constant temperature of $200 \pm 1^\circ$ [1]. Hence the three essential requirements of any DTA instrument used in this test are the maintenance of the DTA cell within 1° of the required constant temperature for at least the duration of the test; the accurate measurement of the sample temperature; and the capability to display this temperature with high resolution. The present investigation has been concerned with an evaluation of the parameters which are critical to the determination of the oxidative induction time (sometimes abbreviated to OIT [1]) of polyethylene.

Experimental

All oxidative stability measurements were carried out on a Stanton Redcroft DTA 671B. The differential temperature is measured by the plate type chromel-alumel thermocouples (see Fig. 1) and a central thermocouple wire permits simultaneous measurement of the sample temperature. The samples were contained in flat, open aluminium pans which allows good contact of the sample with the experimental atmosphere. The desired gas is introduced into the reaction chamber *via* a capillary. The ΔT and sample temperature signals were recorded on a two pen $X_1, X_2/t$ potentiometric recorder.

At 200° the sample temperature chromel-alumel thermocouple output is 8.137 mV with reference to an ice junction at 0° . The required resolution of sample temperature was obtained by backing off with 7.5 mV with a high precision voltage

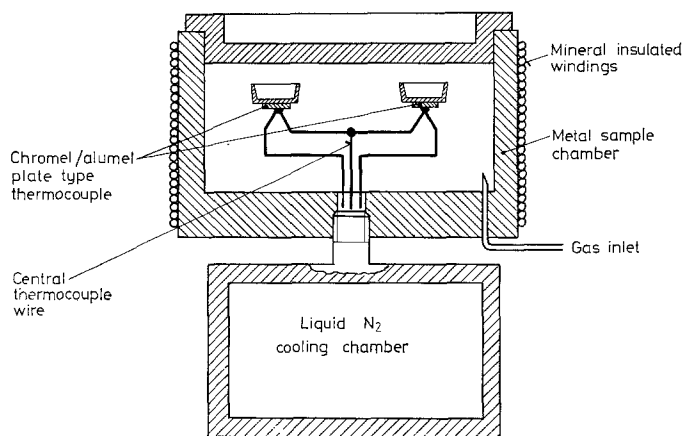


Fig. 1. Schematic of DTA 671B head

source (Time Electronics DC Potentiometer, Model 2003N) and displaying the residual signal at a recorder sensitivity of 1 mV full scale deflection. This enabled the temperature to be measured with an accuracy of 0.05° , and to be monitored for the duration of a test. The potentiometer was also used to carry out regular checks on the recorder sensitivity.

The sample temperature measuring thermocouple was calibrated using the melting points of high purity indium (156.8°) and tin (232.1°). The calibration runs were carried out with the samples sealed in aluminium crucibles at heating rates of 1° min^{-1} .

Stability tests of up to 16 hours on the instrument showed that sample temperature could be maintained to within $\pm 0.3^\circ$ of 200° .

Samples of low density polyethylene containing various antioxidants were used as received. Runs were carried out by heating the DTA head to $200 \pm 1^\circ$ and flushing with nitrogen at 100 ml min^{-1} . A polyethylene disc 5 mm in diameter and 0.3 mm thick, weighing approximately 5 mg, was placed in an aluminium pan and inserted into the DTA head, and held for 5 ± 0.1 minutes. The gas was then changed to oxygen, also at 100 ml min^{-1} , and the oxidation allowed to proceed until the DTA signal (DTA sensitivity $40 \mu\text{V f.s.d.}$) was large enough to drive the pen off-scale. An empty aluminium pan was used for reference purposes.

Results and discussion

A typical run is shown schematically in Fig. 2, which also shows the construction used to measure the induction time. For a polyethylene containing Permanox as antioxidant, a typical set of four consecutive runs gave a mean value of 23.2 ± 0.6 minutes.

A number of important experimental factors were investigated.

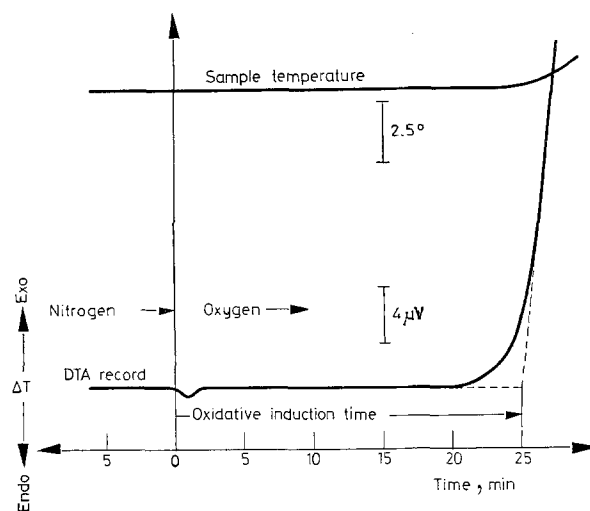


Fig. 2. Schematic DTA and temperature curve for the determination of the oxidative induction time for polyethylene

Sample thickness

Various thicknesses of polyethylene sheet were cut into 5 mm diameter discs and the induction time determined. The results are given in Table 1. It is evident that the 0.1 mm thick samples give a considerably reduced induction time and also show the widest scatter relative to the other results. The tendency for the thicker samples to show increased induction times was also noted.

Table 1

Variation in oxidative induction time with sample thickness

Sample thickness, mm	Sample weight, mg	Sample temperature °C	Oxidative induction time, min
0.1	1.65	199.3	13.5 ± 2.6
0.3	4.91	199.8	23.2 ± 0.6
0.45	7.87	200.0	22.7 ± 1.0
0.75	12.93	199.8	24.6 ± 1.3
1.00	17.53	199.8	26.0 ± 0.9

Each result is the average of at least four determinations

Sample ageing

There is evidence to show that, for a variety of reasons [3], the induction time for polyethylene materials decreases with age [1]. Table 2 gives some results for induction times measured at various time intervals for a sample previously aged

Table 2
Variation of oxidative induction time with sample age

Sample age, weeks	Oxidative induction time, min
12	25.4 \pm 1.1
20	18.7 \pm 0.8
36	17.1 \pm 0.9

Each result is the average of at least four determinations

for twelve weeks, and the noted trend is evident. This implies that for inter-laboratory comparisons to be valid, measurements should be made at similar time intervals after the polymer has been processed. These results also support the previously noted tendency [1] for the change in induction time to decrease with increase in sample age.

Temperature

The variation in induction time was determined over the temperature range 190–212°, and the results are shown in Fig. 3. It is apparent that the induction

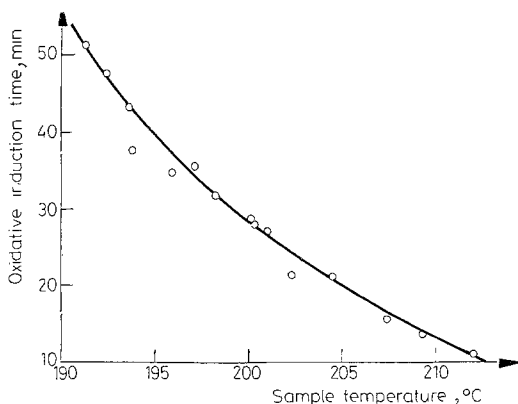


Fig. 3. Variation of oxidative induction time with temperature

time is very dependent on temperature since for this material a change of 1° between 199–201° causes a change of 1.9 minutes. Plots of this kind can be used to normalize experimental results to 200°.

References

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