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A NEW METHOD FOR MEASURING THE INDUCTION PERIOD OF THE OXIDATION OF POLYMERS

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A simple method independent of oxygen absorption measurements was developed for estimating the induction period of the oxidation of polymers. The principle of this method is the estimation of the time in which a sample oxidized at constant temperature exhibits a temperature rise as a consequence of the exothermal effect of the oxidation reaction. The temperature rise is measured as the temperature difference between the sample and a reference material. Results of measurements of induction periods of the oxidation of polymeric substrates inhibited by various antioxidants, obtained both from oxygen absorption measurements and by the new method, are discussed.

The induction period of the oxidation of polymers is usually estimated from oxygen absorption measurements. In some cases these measurements are complicated, due to experimental difficulties or to the conditions of the oxidation test. A simple method independent of oxygen absorption measurements has been developed for these cases.

The principle of this method is the estimation of the time in which a sample oxidized at constant temperature exhibits a temperature rise as a consequence of the exothermal effect of the oxidation reaction. The temperature rise is measured as the temperature difference between the sample and a reference material. This principle was used for the first time by Rudin [1] for the evaluation of antioxidants for polyethylene. In spite of its advantages, the method is not widely used and there have been no further publications dealing with its application.

Apparatus

We tried to develop an apparatus to record curves from samples oxidized under the same conditions as used in oxygen absorption measurements [2], or to obtain both induction period values from one and the same oxidation test. This requirement and the principle of the method led to the apparatus illustrated in Fig. 1.

The sample is placed in an oxidation test tube, practically the same as for oxygen absorption measurements. A chromel-alumel thermocouple is inserted in the sample and connected counterwise to the reference thermocouple placed in a micro test tube close to the test tube with the sample. The reference thermocouple is placed in anhydrous alumina the weight of which is equal to that of the sample. Preliminary experiments showed that application of an inert reference material is not necessary. Compared to differential thermal analysis this technique is not a dynamic thermal process, and therefore the influence of the environment of the reference thermocouple is not significant. For better manipulation we worked without alumina except for testing the influence of certain factors.

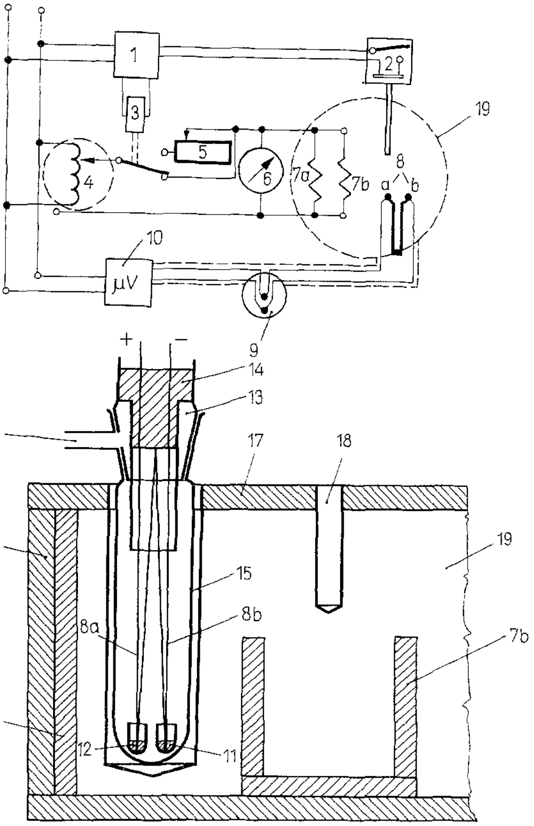

Fig. 1. Scheme of the apparatus. 1 — electronic relay, 2 — contact thermometer, 3 — auxiliary relay, 4 — autotransformer (2.5 A/220 V), 5 — rheostat, 6 — voltmeter (120 V), 7 — heating coil (350 W/220 V), 8 — thermocouples (chromel—alumel, 0.3 mm diameter), 9 — Dewar vessel with cold junctions, 10 — recorder (100 μV/280 mm), 11 — micro test tube with reference thermocouple, 12 — micro test tube with the sample, 13 — ground glass stopper, 14 — the part of glass stopper with thermocouples outlet, cast with silicone rubber, 15 — test tube for oxygen absorption measurements, 16 — side capillary, 17 — thermal insulation, 18 — hole for contact thermometer, 19 — cylindrical aluminium block with eight holes for oxidation test tubes

The constant temperature was maintained by an aluminium heating block with two heating coils. The temperature difference was recorded continuously by a galvanometer. In the steady thermal state during the induction period there is no temperature difference between the tubes, and a base line without deviations is recorded. In the autocatalytic stage of the oxidation the temperature of the sample rises due to the exothermal nature of the oxidation reaction. The temperature difference between the sample and the reference thermocouple is recorded on a chart as a peak (exothermal) (for example see Figs 2 and 3). The induction period is then read off on the time axis at the point of intersection of the base line with the maximum slope of the temperature difference curve.

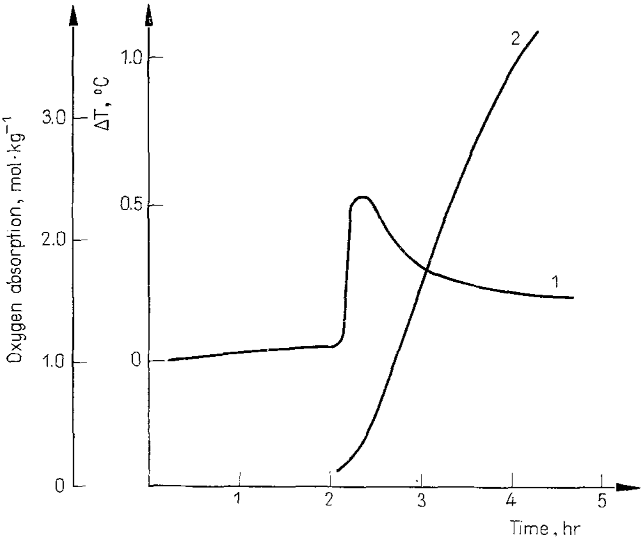

Fig. 2. Thermal curve (1) and oxygen absorption (2) of polyethylene inhibited with 0.1% 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), oxidation at 190°

The essential problem was whether under the given experimental conditions the thermal effect in 10-20 mg samples would be large enough to be detected. Preliminary experiments showed that the temperature differences for average rates of oxidations are of the order of 10^{-10} and in some cases even greater. Since chromel–alumel thermocouples were used with a sensitive recorder (100 μV/280 mm), the corresponding peak values were of the order of centimetres.

Procedure

The oxidation apparatus was evacuated and filled with nitrogen five times and then placed in the heating block. After the operating temperature was reached, the inert atmosphere was replaced by oxygen. On the first oxygen treatment the recorder was switched on. The measurement was run either at a slight overpressure of oxygen (about 20 mm water), or the system was closed by a mercury drop placed in a capillary attached to the side capillary of the oxidation test tube. From the recorder chart the induction period was estimated as described in the previous section.

The reliable estimation of the induction period from curves recorded in tests run under the same conditions as in oxygen absorption made possible the simultaneous estimation of induction periods by both methods. Here both micro test tubes (sample and alumina) were surrounded by granulated soda lime and the inner volume of the oxidation vessel was reduced by a cylindrical glass body fixed to the core of the ground glass stopper. Then a calibrated measuring capillary was connected to the side capillary of the oxidation test tube. The procedure was the same as for oxygen absorption measurement [2], except that the recorder was switched on simultaneously with the replacement of the inert by the oxidative atmosphere.

Evaluation of the method

The estimation of the induction periods of the oxidation of polyethylene and polyethylene-terephthalate inhibited with various types of antioxidant was used to evaluate the method. The results obtained from oxygen absorption measurements and by means of the new method are summarized in Table 1.

The induction period values given in the upper part of the Table were obtained by both methods from the same oxidation tests, and they represent averages of three parallel measurements. Induction periods given in the lower part of the

Table 1

Induction periods estimated by the two methods

Polymer	Inhibitor	Concentration, %	Temperature, °C	IP$-O_2$, hr	IP$-$TR, hr
Polyethylene	1	0.5	180	1.3	1.2
Polyethylene	2	0.5	220	1.4	1.3
Polyethylene-terephthalate	2	0.03	240	1.7	1.6
Polyethylene-terephthalate	3	0.1	240	4.5	4.2
Polyethylene	4	0.05	190	1.0 ± 0.08	0.9 ± 0.1
Polyethylene	4	0.1	190	2.2 ± 0.2	2.1 ± 0.1
Polyethylene	4	0.3	190	6.6 ± 0.1	5.8 ± 0.3
Polyethylene	5	0.3	180	15.9 ± 0.8	17.1 ± 0.7

1 — tris(nonylphenyl)phosphite
2 — N,N′-diphenyl-p-phenylenediamine
3 — 4,4′-dihydroxydiphenyl
4 — 2,2′-methylene-bis(4-methyl-6-tert-butylphenol)
5 — di-β-naphthyl-p-phenylenediamine
IP$-O_2$ — induction periods estimated from oxygen absorption
IP$-$TR — induction periods estimated from the temperature rise

Table were estimated from oxygen absorption measurements and curves recorded separately. In this case 8 parallel measurements were made and the results were evaluated statistically. As can be seen from the Table the two methods give consistent results. In general the values of induction periods estimated from the curves are lower, the difference being constant and independent of temperature, polymer type, stabilizing system and concentration of inhibitor. The probable relative error of both methods is 2–5% for induction periods exceeding two hours and 8–15% for shorter induction periods.

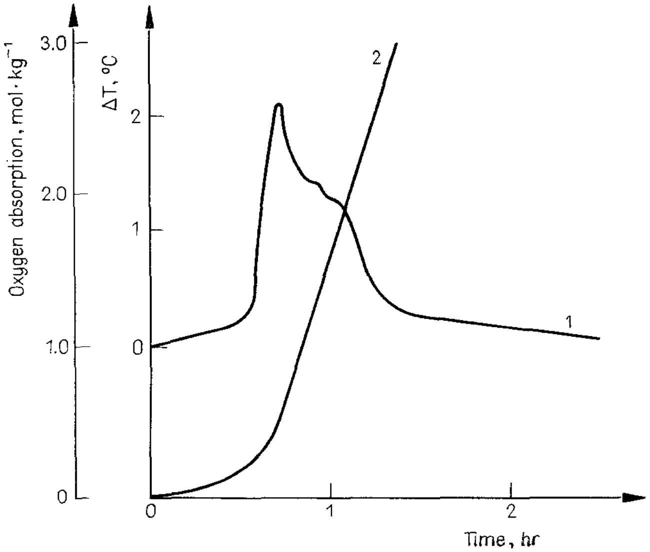

Fig. 3. Thermal curve (1) and oxygen absorption (2) of polyethylene-terephthalate, oxidation at 240°

The measurement of induction periods of oxidation of polymers in the experimental set-up described is not suitable for serial measurements. The elimination of this disadvantage is now under consideration, and we are trying to develop a method for the simultaneous recording of 4–6 curves. Nevertheless, the described procedure was found to be a suitable controlling method for oxygen absorption tests in which the measurement of oxygen absorption is not reliable enough.

References

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2. I. GÖMÖRY, J. ŠTIMEL, R. REYA and A. GÖMÖRYOVÁ, J. Polymer Sci., C 16 (1967) 451.

RÉSUMÉ — On développe une méthode simple et indépendante de la mesure de l'absorption de l'oxygène pour estimer la période d'induction au cours de l'oxydation des polymères. Le principe repose sur l'évaluation du temps pendant lequel un échantillon traité en conditions isothermes manifeste une élévation de température par suite de l'effet exothermique dû à l'oxidation. On mesure l'élévation de température sous forme d'une signal différentiel entre l'échantillon et une substance de référence. On discute les résultats des mesures des périodes d'induction des substrats polymères traités par divers antioxydants, en opérant à l'aide de la nouvelle méthode et par absorption d'oxygène.

ZUSAMMENFASSUNG — Eine von der Sauerstoffabsorption unabhängige Methode wurde zur Messung der Induktionsperiode der Oxydation von Polymeren entwickelt. Sie beruht auf Bestimmung der Zeit, die von einer isothermisch oxydierten Probe erforderlich ist, um einen durch den exothermischen Effekt der Oxydation hervorgerufenen Temperaturanstieg zu zeigen. Der Temperaturanstieg wird als eine Temperaturdifferenz zwischen Probe und Referenzstoff gemessen. Die Ergebnisse von Bestimmungen der durch verschiedene Antioxydanten inhibierten Induktionsperioden von Polymersubstraten durch Sauerstoffabsorption und durch die neue Methode werden besprochen.

Резюме — Для оценки индукционного периода окисления полимеров разработан простой метод, независящий от измерения адсорбции кислорода. Принцип этого состоит в фиксации времени, в течение которого происходит подъем температуры образца, окисленного в изотермических условиях, вследствие экзотермического эффекта реакции окисления. Подъем температуры измеряют как разность температур между образцом и эталоном и поэтому предложен термин «дифференциальная термометрия». Обсуждены результаты измерений индукционного периода полимерных субстратов, ингибированных различными антиоксидантами, полученные как по абсорбции кислорода, так и методом дифференциальной термометрии.