

Processes occurring during the induction period of inhibited oxidation of polyethylene

I. Inhibitor: 2,2'-methylene-bis (4-methyl-6-tert.butylphenol)

Yu. A. Shlyapnikov¹, S. G. Kiryushkin¹, N. K. Tyuleneva¹, M. Iring^{2*}, and Zs. Fodor²

¹Institute of Chemical Physics, USSR Academy of Sciences, SU-117334 Moscow, USSR

²Central Research Institute for Chemistry, Hungarian Academy of Sciences, Pf. 17, H-1525 Budapest, Hungary

SUMMARY

The kinetics of oxygen consumption during the induction period of oxidation of high density polyethylene was studied in the presence of inhibitor 2,2'-methylene-bis(4-methyl-6-tert.butylphenol) within the range 180-220°C. The oxygen consumption curves are complicated, the initial and maximum rates of oxygen consumption pass through minimum with increasing inhibitor concentration. The molecular weight distribution narrows in the course of inhibited oxidation.

Analysis of the regularities found enabled us to distinguish the rates of oxygen consumption by the polymer and by the inhibitor.

INTRODUCTION

The induction period is the first and slow stage of the inhibited oxidation reaction. During this period the essential part of the inhibitor present in the polymer is consumed [1,2] and a marked amount of polymer chains becomes broken [2], but the rate of oxygen consumption remains low. Some papers have been published on the oxygen consumption during induction period in the inhibited oxidation of rubber (for example [3]) while only one was concerned with the oxygen consumption in inhibited polyolefin oxidation [4].

There are two main difficulties concerning the quantitative investigation of oxygen consumption in the presence of inhibitor: the extremely low rate of the process and the formation of volatile products in an amount comparable with that of oxygen consumed. To overcome the first difficulty the reaction volume was decreased to $\sim 6 \text{ cm}^3$ and an oil-filled manometer was used, thus increasing the device sensitivity. To overcome the second difficulty a volatile product absorber (solid KOH) was placed in the cool part of the tube connecting the reactor with the manometer.

EXPERIMENTAL

High density polyethylene was purified by heating the polymer powder in inert atmosphere in a boiling propanol-water (1:1) solution of oxalic acid to remove the traces of metals with subsequent dissolution in boiling m-xylene and precipitation by cooling, then washing with ethanol and vacuum drying. The inhibitor was added to polymer powder with addicton of a small amount of ethanol. The samples were 0.1 cm thick plates prepared by pressing powder at 150°C in nitrogen.

The reaction tube containing the sample (0.100 g) was heated in a thick-wall aluminium cylinder to decrease the temperature gradient,

* To whom offprint requests should be sent

the reaction temperature was kept constant to $\pm 0.35^\circ\text{C}$. The temperature was varied within $180\text{--}220^\circ\text{C}$, the oxygen pressure within $10\text{--}66.7\text{ kPa}$. MMD was measured by gel-chromatography method (1,2,4-trichlorobenzene, 135°C).

RESULTS AND DISCUSSION

As seen from Fig.1.a., the kinetic curves of the pressure change in the reaction volume markedly differed in the absence and in the presence of volatile absorber (solid KOH). Thus in all later experiments an absorber was used to obtain reliable data.

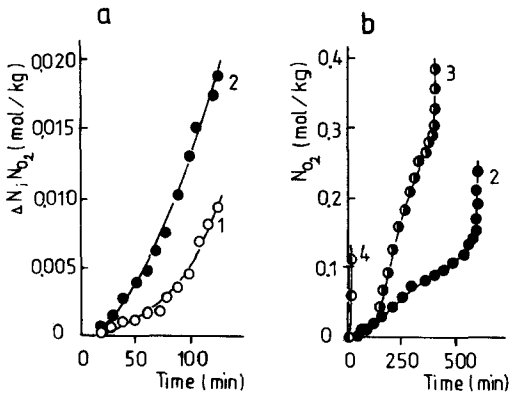


Fig.1.a. The change of overall pressure in the reaction system in the presence of absorber of volatiles (2), $N = V(RT)^{-1}(-\Delta P)$; b. Oxygen consumption in the presence of inhibitor (2), Oxygen consumption in the presence of conversion products of inhibitor (3), and without inhibitor (4). Polyethylene, 200°C , 40 kPa , $i_0 = 0.04\text{ mol/kg}$.

Variation of the sample thickness in the range $0.05\text{--}0.2\text{ cm}$ caused no change in the oxygen consumption curves: the oxygen diffusion does not limit the rate of inhibited oxidation in the experiment. Curves 2. and 4. of Fig.1.b. show the kinetics of oxygen uptake of stabilized and unstabilized PE samples respectively. The effect of decomposition products of stabilizer can be seen on the curve 3 of Fig.1.b. In this experiment sample containing inhibitor was oxidized during 100 min., than cooled. The remaining inhibitor and its volatile conversion products were removed in vacuo (1 hour, 200°C) than the oxidation process was continued. Curve 3. shows that the non-volatile conversion products of inhibitor retard the oxidation in a markedly less degree than the initial inhibitor.

The curves of oxygen consumption in the oxidation of polyethylene containing different concentrations of inhibitor are shown in Fig.2. The curves are of complex shape and some stages can be distinguished (see insert in Fig.2.): at first, the rate of oxygen consumption slowly increases (I.), then passes through maximum (W max), slowly decreases (II.), and sharply increases (III.) to the end of the induction period. The slow increase of the oxidation rate within the induction period and at the beginning of stage III. may be caused by the products of inhibitor conversion. It was seen (Fig.1.b., curve 3.) that the products, non-volatile in vacuum at 200°C , slightly retard the polymer oxidation in the absence of initial form of the inhibitor. When the initial inhibitor concentration exceeds a certain value ($\sim 5 \times 10^{-3}\text{ mol/kg}$) further increase in concentration causes a simultaneous increase in initial and maximum rates of oxygen consumption and of the induction period (Fig.3.).

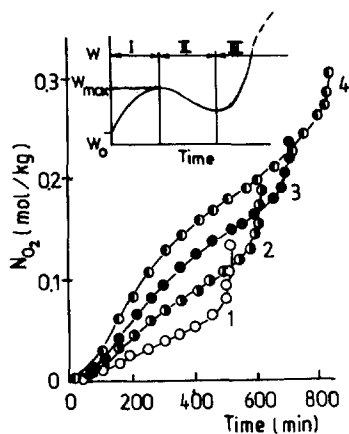


Fig. 2. Oxygen consumption in the course of inhibited polyethylene oxidation at 200°C, oxygen pressure 40 kPa, initial inhibitor concentrations $i_0 = 0.02$ (1), 0.04 (2), 0.06 (3), and 0.08 mol/kg (4).

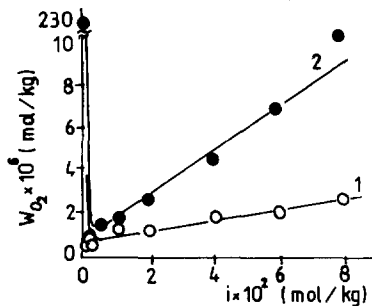


Fig. 3. Initial (1) and maximum (2) rates of oxygen consumption as functions of initial inhibitor concentration. 200°C, oxygen 40 kPa.

The initial and maximum rates of oxygen consumption as functions of the inhibitor concentration are shown in Fig. 3. Both dependences are presented by curved lines with minima, the right branches possess straight-line asymptotes.

Fig. 4. shows the kinetic curves of oxygen consumption in polyethylene oxidation at the same inhibitor concentration (0.04 mol/kg), but at different oxygen pressures. The increase in oxygen pressure results in a higher initial rate of oxygen consumption and in decrease of the induction period.

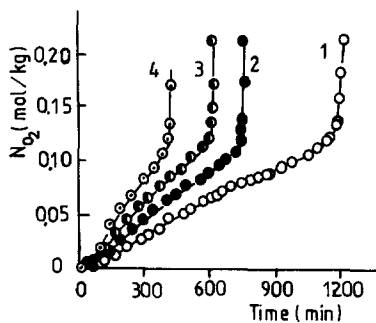


Fig. 4. Kinetic curves of oxygen consumption at 200°C, initial inhibitor concentration 0.04 mol/kg, and various oxygen pressures: 10 (1), 20 (2), 40 (3), and 66.7 kPa (4).

The pressure dependences of initial and maximum rates are presented in Fig. 5. Within the range of 10-66.7 kPa these dependences are presented by straight lines (which do not cross the coordinate origin).

carbonyl- and alcohol-hydroxyl groups are not shown in the scheme since the low concentration of these groups formed in the induction period influence negligibly the reactivity of the polymer as a whole.

The following equations for free radical and hydroperoxide group balance are derived from scheme (1):

$$\frac{d([R'] + [RO_2'])}{dt} = f_o k_o [RH] [O_2] + f_i k_{oi} [O_2] + \sigma k_4 [RH][ROOH] - k_3 i [RO_2'] \quad (2)$$

$$\frac{d[ROOH]}{dt} = \alpha k_2 [RH][RO_2'] + k_3 i [RO_2'] - k_4 [RH][ROOH] \quad (3)$$

(here $i = [IH]$). Using the method of Bodenstein we assume $d([R'] + [RO_2'])/dt = 0$. At high temperature the rate of reaction (2) and that of reaction (4) are commensurable and one may assume that $d[ROOH]/dt = 0$. Solving the algebraic equations obtained we find the expression for the free radical RO_2' concentration

$$[RO_2'] = \frac{(f_o k_o [RH] + f_i k_{oi}) [O_2]}{(1 - \sigma) k_3 i - \alpha \sigma k_2 [RH]} \quad (4)$$

This expression is valid only when the denominator of (4) is positive, i.e. when $i > i_{cr}$, where i_{cr} is the critical inhibitor concentration

$$i_{cr} = \frac{\alpha \sigma k_2 [RH]}{(1 - \sigma) k_3} \quad (5)$$

Assuming that the reaction $R' + O_2$ is equal to the rate of interaction of RO_2' with RH, we get:

$$k_1 [R'] [O_2] = k_2 [RO_2'] [RH]$$

Neglecting the rates of free radical formation and oxygen consumption in reaction O compared to O^* in scheme (1) we get the expression for the rate of oxygen consumption by the oxidizing polymer

$$(W_{O_2})_P = \frac{f_i k_{oi} k_2 [RH] [O_2] i}{(1 - \sigma) k_3 i - \alpha \sigma k_2 [RH]} = \frac{f_i k_{oi} k_2 [RH] [O_2] i}{(1 - \sigma) (i - i_{cr}) k_3} \quad (6)$$

When the oxidation of one inhibitor molecule takes ϵ molecules of oxygen, the rate of oxygen consumption in direct inhibitor oxidation will be

$$(W_{O_2})_i = \epsilon k_{oi} [O_2] i \quad (7)$$

Adding (6) and (7) together we find the overall rate of oxygen consumption in inhibited polymer oxidation

$$W_{O_2} = (W_{O_2})_p + (W_{O_2})_i = \left[\frac{f_i k_2 [RH]}{(1 - \sigma)(i - i_{cr})k_3} + \epsilon \right] k_{oi} [O_2] i \quad (8)$$

Expression (8) is in good agreement with experimental data obtained for polyethylene oxidation in the presence of inhibitor. This expression gives a curve with a minimum, and two straight-line asymptotes: $W_{O_2} \rightarrow \infty$ if $i \rightarrow i_{cr}$, and if $i \gg i_{cr}$ then $W_{O_2} = f_i k_2 [RH] [O_2] (1 - \sigma)^{-1} k_3^{-1} k_{oi}^{-1} i$

+ $\epsilon k_{oi} [O_2] i$. The point of intersection of the second asymptote with the ordinate axis corresponds to minimum rate of oxygen consumption by the polymer as such, and the slope is $\epsilon k_{oi} [O_2] = 2.3 \times 10^{-5} \text{ s}^{-1}$ for the initial and $1.03 \times 10^{-4} \text{ s}^{-1}$ for the maximum rates.

According to (8) the rate of oxygen consumption must be directly proportional to its concentration, i.e. to the oxygen pressure over the polymer. Some deviations observed for low oxygen pressures (Fig.5.) are due to contribution of the reaction of radical $R\cdot$ with IH and I' . This has not been considered in scheme (1).

The inhibitor is consumed in reactions with radicals $RO_2\cdot$ and with oxygen. Correspondingly the rate of its consumption is equal to the sum of rates of these two reactions, i.e.

$$-\frac{di}{dt} = q_i^{-1} k_3 [RO_2\cdot] i + k_{oi} [O_2] i = \left[\frac{f_i i}{(1 - \sigma)(i - i_{cr})q_i} + 1 \right] k_{oi} [O_2] i = k_{eff} i \quad (10)$$

where q_i is the stoichiometric coefficient of inhibition. According to (10) at $i \gg i_{cr}$ the inhibitor consumption is first order in concentration

($k_{eff} = \text{const.}$) but when the concentration approaches the critical value this law becomes violated and the observed rate constant increases. As seen from Fig.7. at an initial inhibitor concentration 0.04 mol/kg and $i/i_{cr} = 30$ the first order law is obeyed up to 85 % of the inhibitor conversion.

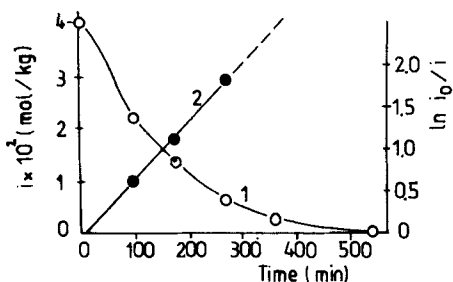


Fig.7. Inhibitor consumption during induction period of polyethylene oxidation plotted in the usual (1) and semi-logarithmic coordinates (2). 200°C, 40 kPa, $i_0 = 0.04 \text{ mol/kg}$.

The observed rate constant of inhibitor consumption at 200°C and oxygen pressure $P_{O_2} = 40 \text{ kPa}$ is $k_{eff} = 1.13 \times 10^{-4} \text{ s}^{-1}$. This value is essentially lower than that at the same temperature and oxygen pressure in experiments that do not involve removing of the volatiles ($\sim 3 \times 10^{-4} \text{ s}^{-1}$). The difference can be attributed to the different topological structures of the samples studied, i.e. to the fact that the properties of a polymer depend on the character of polymer chain entanglement in it.

Thus the results obtained for oxygen consumption in the induction period of inhibited oxidation confirm the mechanism proposed earlier [1,2,5].

The minimum rate of oxygen consumption in the oxidation of polymer as such is expressed by the first term in (9). When calculated from the data on initial oxidation rate at 200°C, 40 kPa, this rate was close to 7×10^{-7} mol/kg s and only slowly changed with temperature, whereas that calculated from the maximum rate virtually did not change. The activation energy of inhibitor oxidation calculated from the temperature change of the second term in (9) was 117 kJ/mol, and practically coincided with that calculated from k_{eff} (121 kJ/mol [6]).

The symbols k_0 , f_1 , and k_3 in the first term of (9) characterize antioxidative efficiency of the inhibitor when the latter has no effect on G - the free radical yield in the hydroperoxide group decomposition.

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