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Calculations

Kinetic Evaluation of Polyethylene Autoxidation in Melt

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Summary

This work proposes a description of the kinetics of polyethylene autoxidation in melt. The model takes into consideration the effect of neighbouring groups on the hydroperoxide decomposition. Using the proposed model, reliable constants can be calculated for the autoxidation of polyethylene.

Introduction

In the extensively studied field of polyolefin oxidation relatively little work has been done to describe the kinetics of the process. Main works in kinetic description of the autoxidation (PUDOV et al. 1963, CHIEN and BOSS 1967, IRING et al. 1974, DENISOV 1978) accepted a simplified mechanism with degenerate chain branching, developed for liquid phase hydrocarbon oxidation (EMANUEL' et al. 1965). In the above papers only one type of hydroperoxide decomposition was assumed as dominating radical producing process. In case of polyethylene, this was a simple unimolecular decomposition of polyethylene hydroperoxide (PEHP).

However, investigations of decomposition of polyolefin hydroperoxides have proved that this is a complex process (CHIEN 1968, IRING et al. 1976, SHLYAPNIKOV et al. 1979). In the present publication an attempt is made to describe the time dependence of oxygen uptake and hydroperoxide concentration during PE oxidation, taking into consideration that the hydroperoxide decomposition has a more complex mechanism.

Experimental

LDPE (Tipolen FA 221o, kindly supplied by Tisza Chemical Works, Hungary) was oxidized in melt at 13o, 15o, and 16o°C and O_2 pressure of 1oo kPa. The polymer was characterized in a previous paper (IRING et al. 1974). Experimental methods were desribed by IRING et al. (1974, 1975).

During oxidation, the overall oxygen uptake ($[O_2]$) was followed. At the end of the oxidation, the hydroperoxide concentration of the oxidized sample ($[ROOH]$) was determined and the rate of oxygen uptake ($d[O_2]/dt=W_{O_2}$) was calculated.

Results and Discussion

Figures 1 and 2 show the time dependence of oxygen uptake and hydroperoxide concentration, respectively. It is noticeable that the hydroperoxide concentration decreases rapidly after reaching a maximum. The maximum hydroperoxide concentration belongs to a lower conversion than the maximum rate of oxygen absorption (see also Fig.3). Figure 3 also shows that W_{O_2} values belonging to the same hydroperoxide concentration are considerably higher in the decelerating than in the accelerating region of oxidation.

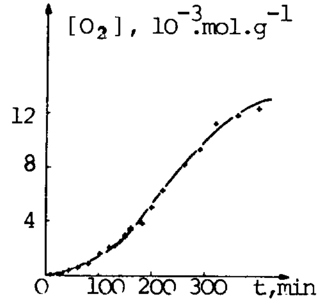

Figure 1
Time dependence of oxygen absorption during polyethylene autoxidation (150°C, 100 kPa)

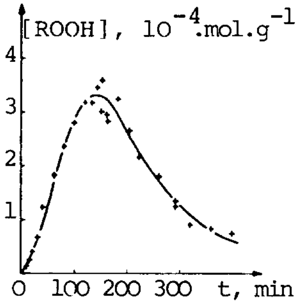

Figure 2
Time dependence of hydroperoxide concentration during polyethylene autoxidation (150°C, 100 kPa)

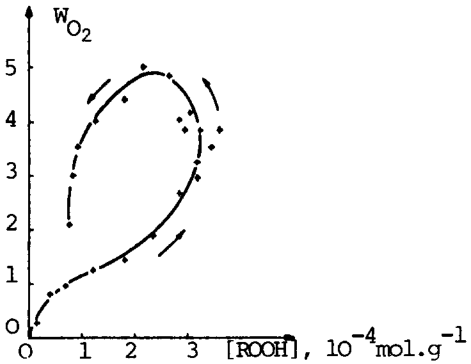

Figure 3
Relationship between the rate of oxygen uptake and the hydroperoxide concentration during polyethylene oxidation (150°C, 100 kPa) Arrows indicate increasing conversion

Investigation of liquid phase hydrocarbon oxidation proved that oxygen containing functional groups (carbonyl, carboxyl, hydroxyl, etc.) accelerate the decomposition of hydroperoxides (EMANUEL' et al. 1965, HIATT 1971). Similar conclusion was drawn by CHIEN (1968) for PEHP. However, SHLYAPNIKOV et al. (1979) found slower hydroperoxide decomposition in the presence of other functional groups in oxidized polypropylene.

In the forthcoming kinetic description two types of decomposing hydroperoxides are considered: "free" ($ROOH_f$) and "bonded" ($ROOH_b$). The latter are hydrogen bonded to functional groups formed during the oxidation and decompose at a different rate than the former. Assuming an equilibrium between the two types of hydroperoxides, we have:

$$[ROOH_b] = K'_a[ROOH_f][FG] \qquad (1)$$

$$[ROOH_f] = \frac{[ROOH]}{1+K'_a[FG]} \qquad (2)$$

Here K'_a stands for the equilibrium constant, and [FG] is the concentration of those functional groups which accelerate hydroperoxide decomposition.

As a first approximation, a direct proportionality between [FG] and the absorbed oxygen is assumed, i.e., $K'_a[FG] = K_a[O_2]$. This assumption is supported by the observation that there is a direct proportionality between $[O_2]$ and the amount of oxygen in functional groups IRING et al.[1982].

There is another experience we wish to take into consideration, namely that the rate of hydroperoxide formation is lower than the rate of oxygen uptake (BUCHACHENKO 1976, SHILOV and DENISOV 1977).

Some approximations of the earlier model of PUDOV et al. (1963) were considered in our calculations as well:

— Primary initiation is negligible as compared to the radical formation in hydroperoxide decomposition, from the beginning of the oxidation.

— Radicals formed during hydroperoxide decomposition are highly reactive and produce alkyl radicals in fast reactions.

— At atmospheric oxygen pressure, alkyl radicals transform to alkylperoxy radicals in a fast reaction. This reaction is not rate-determining; other reactions of alkyl radicals can be neglected.

— As a primary approximation, the concentration of radicals participating in polyethylene oxidation is considered quasi-stationary from the beginning of the oxidation.

The suggested mechanism is the following:

$$ROOH_f \xrightarrow{k'_3} \{RO^{\bullet}+{}^{\bullet}OH\} \xrightarrow[\delta' O_2]{\delta' RH} \delta' RO_2^{\bullet} + \text{stable products} \qquad (3)$$

$$ROOH_b \xrightarrow{k''_3} \{RO^{\bullet}+{}^{\bullet}OH\} \xrightarrow[\delta'' O_2]{\delta'' RH} \delta'' RO_2^{\bullet} + \text{stable products} \qquad (4)$$

$$RO_2^\bullet + RH\ (+O_2) \xrightarrow{k_2} RO_2^\bullet + \alpha ROOH + \text{oxygen containing products} \qquad (5)$$

$$RO_2^\bullet + RO_2^\bullet \xrightarrow{k_4} \text{stable products} + O_2 \qquad (6)$$

δ' and δ'' show the number of oxidation chains per one decomposed free and bonded hydroperoxide molecule, respectively, and $\alpha \equiv \frac{\text{rate of hydroperoxide formation}}{\text{rate of oxygen absorption}}$. α is supposed to remain constant.

The corresponding differential equations are as follows:

$$\frac{d[RO_2^\bullet]}{d\,t} = \delta' k_3'[ROOH_f] + \delta'' k_3''[ROOH_b] - 2k_4[RO_2^\bullet]^2 \qquad (7)$$

$$\frac{d[ROOH]}{d\,t} = \alpha k_2[RH][RO_2^\bullet] - k_3'[ROOH_f] - k_3''[ROOH_b] \qquad (8)$$

$$\frac{d[O_2]}{d\,t} = k_2[RH][RO_2^\bullet] + \delta' k_3'[ROOH_f] + \delta'' k_3''[ROOH_b] - k_4[RO_2^\bullet]^2 \qquad (9)$$

Because of the stationarity, we have:

$$\delta' k_3'[ROOH_f] + \delta'' k_3''[ROOH_b] \approx 2k_4[RO_2^\bullet]^2 \qquad (1o)$$

i.e., Eq. 9 can be written in the form

$$\frac{d[O_2]}{d\,t} = k_2[RH][RO_2^\bullet] + k_4[RO_2^\bullet]^2 \qquad (11)$$

In case of kinetic chain length $\nu > 5$, the second term of Eq. 11 can be neglected.

In our further treatment, for lack of direct information about the value of δ' and δ'', we use the assumption of $\delta' \approx \delta'' \approx \delta$. Under stationary conditions, assuming that $[RH]=[RH]_o-[O_2]$, we have:

$$\frac{d[O_2]}{d\,t} = k_2[RH]_o\left(1-\frac{[O_2]}{[RH]_o}\right)\sqrt{\frac{\delta[ROOH](k_3'+k_3''K_a[O_2])}{2k_4(1+K_a[O_2])}} \qquad (12)$$

$$\frac{d[ROOH]}{d\,t} = \alpha\frac{d[O_2]}{d\,t} - \frac{k_3'+k_3''K_a[O_2]}{1+K_a[O_2]}[ROOH] \qquad (13)$$

Equations (12) and (13) were integrated numerically using a Runge-Kutta routine for different values of $\delta k_2^2[RH]_0^2(2k_4)^{-1}$, k_3', k_3'' and K_a. α has been determined using the value of $\frac{[ROOH]}{[O_2]}$ extrapolated to t=o. The best fit to the measured curves (Fig. 4-6) was achieved with the values shown in Table 1.

Knowing the oxidizability $\{k_2[RH]_0(2k_4)^{-1/2}\}$, further important constants can be calculated using $\delta^{1/2}k_2[RH]_0(2k_4)^{-1/2}$. Oxidizability was determined in initiated oxidation (VÁGÓ et al.), its extrapolated values are given in Table 1. The calcu-

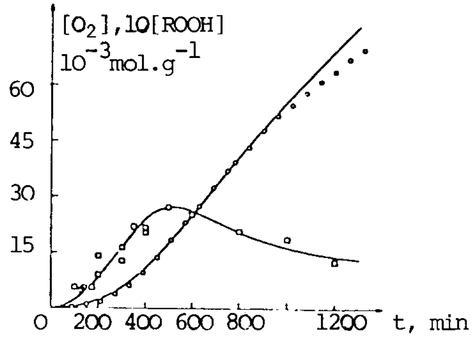

Figure 4
Comparison of measured and calculated values at 13o °C
Experimental: absorbed oxygen (o), accumulated hydroperoxide
(□); calculated: ——.

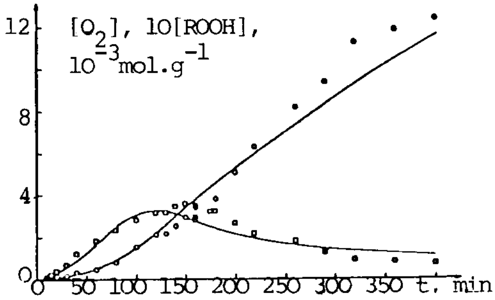

Figure 5
Comparison of measured and calculated values at 15o °C
Experimental: absorbed oxygen (o), accumulated hydroperoxide
(□); calculated: ——.

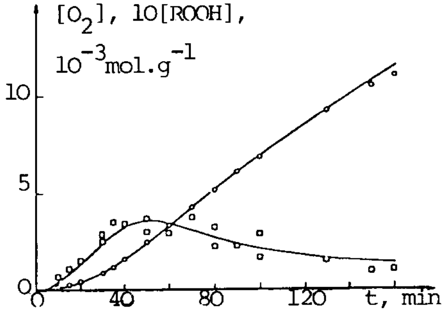

Figure 6
Comparison of measured and calculated values at 16o °C
Experimental: absorbed oxygen (o), accumulated hydroperoxide
(□); calculated: ——.

lated δ values (Table 1) are in good agreement with that of CHIEN (1968).

TABLE 1

Constants used in the kinetic description of polyethylene autoxidation

T, °C	130	150	160
α	0.44	0.44	0.45
$\delta^{1/2}k_2[RH]_0(2k_4)^{-1/2}$, $mol^{1/2}.g^{-1/2}.min^{-1/2}$	4.2×10^{-3}	9.5×10^{-3}	14.7×10^{-3}
k_3', min^{-1}	2.5×10^{-3}	1.1×10^{-2}	3.5×10^{-2}
k_3'', min^{-1}	0.034	0.17	0.38
K_a, $g.mol^{-1}$	230	150	120
$k_2[RH]_0(2k_4)^{-1/2}$, $mol^{1/2}.g^{-1/2}.min^{-1/2}$	7.4×10^{-3}	1.7×10^{-2}	2.6×10^{-2}
δ	0.3	0.3	0.3
$\nu_{W_{O_2},max}$	7	7	7

The kinetic chain length (ν) was calculated from the following equation:

$$\nu = \frac{W_{O_2}(1+K_a[O_2])}{\delta[ROOH](k_3'+k_3''K_a[O_2])} \qquad (14)$$

Since ν changes during the oxidation, its values given in Table 1 were estimated at $W_{O_2,max}$.

The Arrhenius plot of k_3', k_3'' and K_a can be seen in Fig. 7 and 8. The reaction heat calculated for formation of bonded hydroperoxide is -31 $kJ.mol^{-1}$ (-7.5 $kcal.mol^{-1}$). The activation energy of the decomposition of free and bonded hydroperoxide was found to be 124 $kJ.mol^{-1}$ (30 $kcal.mol^{-1}$) and 116 $kJ.mol^{-1}$ (28 $kcal.mol^{-1}$), respectively. The k_3' and k_3'' values measured by Chien fall quite well on our Arrhenius plot.

It can be established that the constants calculated using the model formulated in Eqs. (1)-(6) do not contradict to their physical meaning and are in good agreement with data of several other authors. The calculated curves of $[O_2]$ vs. t and [ROOH] vs. t fairly describe the experimental data up to considerable conversion. There are some differences, especially at high conversion, which indicate the complex nature of polyethylene oxidation, and makes it worth considering whether there are some other reaction steps playing more important role in polyethylene oxidation.

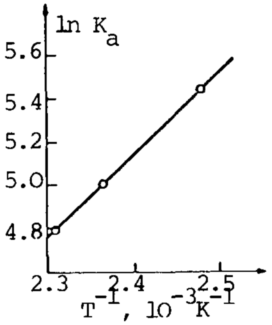

Figure 7
Temperature dependence of equilibrium constant for bonded hydroperoxide

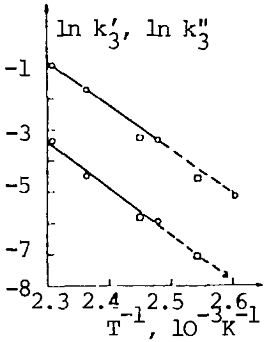

Figure 8
Temperature dependence of the rate constants of decomposition of free (a) and bonded (b) hydroperoxide, respectively
□ CHIEN's data (1968)

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