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Reactions

The effect of reaction conditions on LDPE oxidation

M. Iring[1], Zs. Fodor[1], K. Barabás[1], T. Kelen[1,2], and F. Tüdős[1,3*]

[1]Central Research Institute for Chemistry, Hungarian Academy of Sciences,
P.O. Box 17, H-1525 Budapest, Hungary

[2]Institute of Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen 10, Hungary

[3]Department of Chemical Technology, Eötvös Loránd University, Muzeum krt. 6–8,
H-1088 Budapest, Hungary

SUMMARY

The formation kinetics of functional groups and the kinetics of the molecular mass change were investigated in low density polyethylene oxidized under different conditions in static and dynamic equipments. The processes studied were found highly sensitive to the oxygen supply. With the increase of $[O_2]$ higher rate of oxidation and increasing fragmentation can be observed. If $[O_2]$ is reduced, crosslinking will dominate. Mechanical effect was significant only during the melting of the polymer. Under dynamic conditions, diffusion control was always found.

INTRODUCTION

The knowledge of the mechanism of polyethylene oxidation in the melt is important also in respect of the practical problems connecting with the application of the polymer. The change of the composition of oxidation products induced by simultaneous thermooxidative degradation and intensive mechanical stress has been studied as well [1-10]. The oxidation mechanism is supposed to be the same in both cases. The differences in the product distribution are attributed by Adams [2] to the different degradation temperatures applied in the two series of measurements. Fragmentation and long chain branches formation as well as crosslinking depend on the oxidation conditions. The effect of shearing has been differently evaluated by the different authors [3,5,7].

The aim of the present work is to investigate the connection between the reaction conditions and some main features of the oxidation. We wanted to clarify the effect of shear. The oxidation of LDPE was studied both under static conditions and in a mixing chamber, with possibly commensurable partial O_2 pressure and temperature. The kinetics of oxygen-containing functional group formation and the molecular mass change were investigated.

EXPERIMENTAL

Low density PE of the type Typolen FA 2210 characterized earlier [11] was used in the experiments. Film samples pressed from re-precipitated powder or from commercial granulate were applied. The static degradation was carried out between 130 and 180 °C at 100 kPa (760 Torr) and 2.7 kPa (20 Torr) O_2 pressure. The dinamic measurements were carried out in a mixing chamber (of approx. 50 cm^3 volume) of a Haake-Rheocord instrument, using

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[*] To whom offprint requests should be sent

three different methods: closed chamber, introduction of air and introduction of oxygen (see Table 1). It is to be noted that the polymer was warmed up by the viscosity dependent mixing work, thus the reaction did not proceed under strictly isothermal conditions. The mixing was mostly carried out with 100 rpm, other values are indicated.

Table 1

Conditions of degradation

static equipment	20-30 µm thick films
temperature:	130-160 °C
oxygen pressure:	2.7 kPa (20 Torr)
	100 kPa (760 Torr)
Mixing chamber (Rheomix 600), 35 g feed	
temperature 130-180 °C, 25-100 rpm	
1.) closed chamber	air oozing in
2.) air stream	10 l/h
3.) oxygen stream	10 l/h

Characteristics investigated

(For description of the investigating methods see [12-14].)

concentration of -OOH, =CO, -COOH, -COOR groups (IR; titration)

molecular mass: $\overline{M}_n$, $\overline{M}_w$ (GPC)

gel content: G (extraction)

The amount of hydroperoxides formed during degradation was measured iodometrically [12]. By simultaneous use of IR spectroscopy and acidimetric titration, the amount of acid and keton groups, and the total concentration of ester and lactone groups ([COOR]) were determined [13]. Gel content of the samples was calculated from the data of their extraction with xylene. The molecular mass change was followed by GPC [14]. In static oxidation, the oxygen uptake was also measured. The instrument used for dynamic oxidation is not suitable for this kind of measurements.

EXPERIMENTAL RESULTS

The main product of the initial stage of oxidation is the hydroperoxide which undergoes decomposition initiating new oxidation chains, thus its quantity strongly affects the rate of oxidation. According to our measurements, in static system the maximum of [-OOH] vs. t function is only slightly influenced by the raise of the temperature (see Fig.1), however, the time, required to reach the maximum decreases. The reduction of oxygen pressure (from 100 kPa to 2.7 kPa) decreases $[-OOH]_{max}$ and increases the time required to reach it.

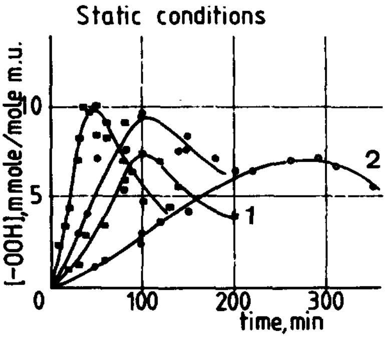

Fig.1. The change of hydroperoxide concentration in static oxidation of 20-30 µm thick films. ■ 160°C, ~ 100 kPa O_2; ● 150°C, ~ 100 kPa O_2; □ 160°C, ~ 2.7 kPa O_2,-1-; o 150°C, 2.7 kPa O_2,-2-.

For kneaded samples, the hydroperoxide content is lower and the time required to reach the maximum is longer than for samples oxidized in the same atmosphere in a static equipment as can be seen comparing Figures 1 and 2.

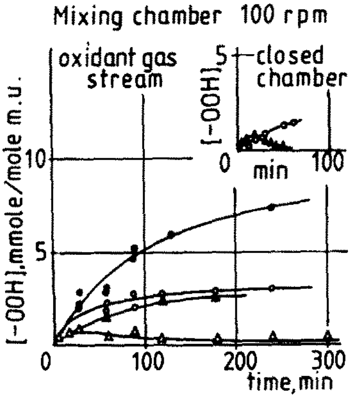

Fig.2. The change of hydroperoxide concentration in dynamic oxidation. In closed chamber: o ~140°C, Δ~180°C. In oxidizing gas stream: ● O_2 10 Lit/h, 160 ÷150°C; o air 10 Lit/h, 160-150°C; ▲ O_2 10 Lit/h 178 ÷ 170°C; Δ air 10 Lit/h, 178-170°C.

The hydroperoxide content strongly decreases with increasing temperature (see Fig.2). (The tendency is similar to that observed by Chakraborty [3], although the kinetics are significantly different.) The explanation for this is that a lower oxygen concentration is present in a polymer when it is oxidized in a mixing chamber than in the film samples. At higher temperatures, the diffusion control becomes more and more pronounced because the rate of oxidation increases.

The oxygen supply of the system decreases in the following order: in oxygen stream > in air stream > in closed mixing chamber.

In a "closed" mixing chamber the oxygen is supplied only through the tight places of the chamber thus the supply is poor. At lower temperatures when the rate of -OOH decomposition requiring a relatively high activation energy is small, a temporal increase of [-OOH] is observed. At higher temperatures, the -OOH groups decompose almost instantaneously, but no sufficient oxygen is available for their regeneration, therefore [-OOH] becomes constant at an extermely low level after an initial maximum. The worse the oxygen supply of the system, the earlier can the maximum be observed. In many cases, the investigated mixing time was too short to reach the maximum.

In the molecular mass change, also a remarkable difference can be observed between oxidations in static environment or in mixing chamber. The process is illustrated by the time dependence of the number of chain scissions ($s = (\bar{M}_{n,o}/\bar{M}_{n,t}) - 1$) which can be calculated from GPC data no crosslinking occurs. In purely thermal oxidation, the chain scission vs. time function has an induction period (see Fig. 3) and is of accelerating character, similarly to the oxygen uptake. If, however the degradation is carried out in a mixing chamber in oxygen stream, the chain scission is the fastest in the initial stage, as illustrated by Fig.4.

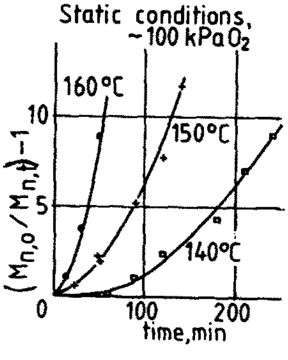

Fig.3. Temperature and time dependence of chain scissions in static oxidation of 20 ÷ 30 µm thick films.

The difference suggests that in the period of melting of the polymer, also the shear effect caused by intensive mixing can induce chain scission, thus contributing to the initiation of the oxidation process. Since in the later stage of degradation, in addition to fragmentation also molecular mass

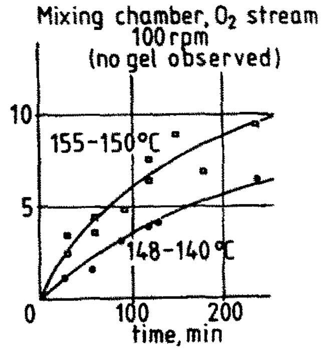

Fig.4. Temperature and time dependence of chain scissions in degradation carried out in mixing chamber in 10 Lit/h O_2 stream.

increasing reactions take place and the two processes cannot be separately investigated, the effect of shear on the degradation of already molten polymer cannot be determined.

At a low oxygen concentration, only part of the alkyl radicals appearing after the decomposition of hydroperoxides can react with oxygen and form new hydroperoxides. Other alkyl radicals undergo other competitive reactions, e.g., recombination which results in crosslinking and molecular mass increase. The worse is the oxygen supply the more intensive is the crosslinking. If the degradation was carried out in a closed mixing chamber (see Fig.5) or in air stream, there was always crosslink fromation, but it could be observed also under static conditions, at an oxygen pressure of 2.7 kPa.

To illustrate the changes in the molecular mass, Fig.5 shows the change of gel content (G) in time and of mass average molecular mass ($\overline{M}_w$), together with the change of the torque (M) necessary to the constant speed mixing. The torque depends on the viscosity, i.e., on the molecular mass and on the temperature of the melt.

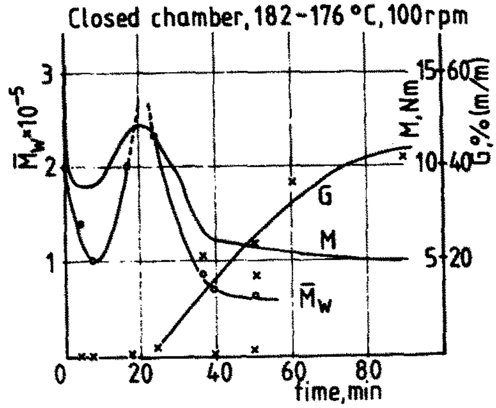

Fig.5. The changes in torque (M), mass average molecular mass ($\overline{M}_w$), and gel content (G) during degradation carried out in closed mixing chamber.

As can be seen in the figure, $\overline{M}_w$ increases after an initial decrease, in the gel point theoretically infinitely. Than the average molecular mass of the soluble part decreases and the gel content increases. These effects give a maximum followed by a decrease in the torque curve. With introduction of oxygen, no crosslinking could be observed in the mixing chamber below 160°C. For these measurements, no torque maximum could be observed. However, transitional slow down of the torque decreases suggests that there are some reactions too which increase the molecular mass (see Fig. 6.).

During degradations, oxygen incorporates in the form of different functional groups into the polymer. The total amount and the distribution among different kinds of groups is affected by the amount of oxygen getting into the polymer. Under dinamic conditions, it can be increased also by the intensity of mixing. Higher speed renew more rapidly the surface of the melt and shortens the way of diffusion, thus the process is less diffusion controlled. This is illustrated by the dependence of the total oxygen uptake (O_p) on the mixing speed in the degradation in closed mixing chamber (see Fig.7). The value of O_p was calculated from the experimental data using the following relationship:

$$O_p = [-OOH] + [-COOH] + [-COOR] + 1/2[=CO], \text{ mmole } O_2/\text{mole } C_2H_4$$

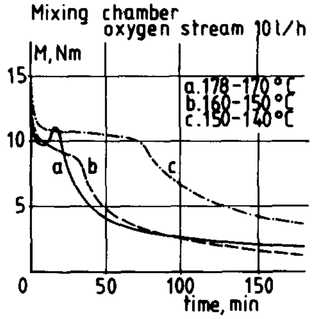

Fig.6. The change in torque (M) during oxidation in mixing chamber at different temperatures and O_2 streams.

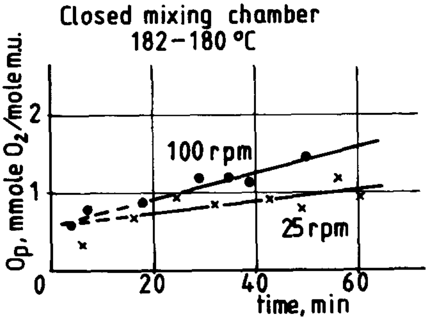

Fig.7. Dependence of total amount of oxygen incorporated into the polymer on mixing speed for oxidation in closed mixing chamber.

While at the beginning of the reaction, hidroperoxide predominate among the oxygen containing functional groups, later the carbonyl groups accumulate in the polymer and their concentration monotonously increases. Fig.8 shows experimental data of two series of experiments. For one of them oxygen, for the other air was introduced into the chamber above the polymer, the other conditions were the same.

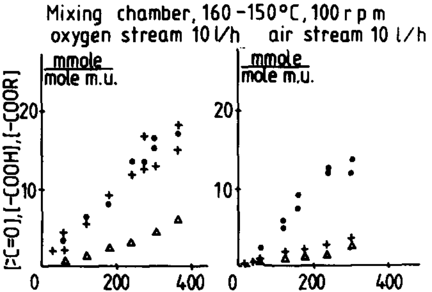

Fig.8. Time dependence of formation of some oxygen containing functional groups on mixing chamber flushed with O_2 or with air.

The increase of the amount of oxygen concentration the atmosphere in the chamber makes more C=O containing group form during the same time. The least sensitive to the oxygen content is the rate of ketone group formation. The [-COOR]/([CO] + [-COOH]+ [-COOR]) ratio was less influenced by the partial pressure of oxygen which, however strongly affected the rate of acid formation. This is demonstrated also by Fig.9 which shows the acid formation kinetics in static equipment and in mixing chamber.

Comparison of the curves suggests that better oxygen supply favours acid formation. This can be achieved by using thin polymer sample and sufficient concentration of oxygen.

The observation can be well interpreted considering the generally accepted fact that the acid formation is bound to the presence of alkylperoxy radicals, the appearance of which is favoured by higher oxygen concentration. One of the possible ways leading to the formation of carboxyl groups is the isomer-

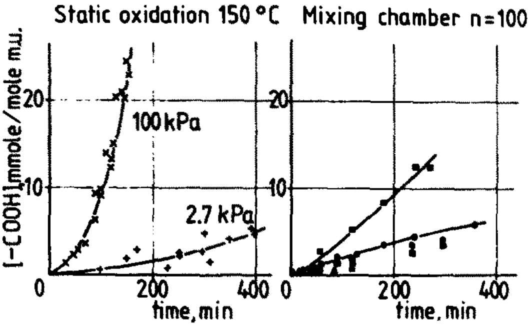

Fig.9. Time dependence of carboxyl group formation under different degradation conditions. The thickness of films is 20÷30 μm in static oxidation. In mixing chamber: △ 140÷136°C, closed; o 148÷140°C, 10 Lit/h O_2; □ 155÷150°C, 10 Lit/h air; ● 148÷140°C, 10 Lit/h O_2, ■ 155÷150°C 10 Lit/h O_2

ization of the alkylperoxy radicals [15]. Further oxidation of aldehyde groups results also in acid formation.

The kneaded samples underwent yellowish discoloration in all casses suggesting the presence of double bonds. Their quantity was not measured. The extent of the discoloration is in reciprocal relationship with the oxygen supply.

CONCLUSIONS

The characteristics of oxidation proceeding under static and dynamic conditions are summarized in Table 2.

Table 2
Main differences found in the characteristics of PE oxidation

	In static equipment at high oxygen pressure	In mixing chamber
Main feacture	Mainly kinetically controlled	Mainly diffusion controlled
Change in molecular mass	Rate of chain scissions increases during degradation	Rate of chain scissions decreases during degradation; considerable crosslinking occurs
Hydroperoxide kinetics	Concentration curve has a maximum; $[-OOH]_{max}$ is independent of temperature	Mostly monotonously increasing concentration curve: $[-OOH]_{max}$ decreases with increasing temperature, increases with speed of mixing
Carbonyl kinetics	Concentration curve with accelerating character	Rate of formation is nearly constant, increases with speed of mixing

Investigating the effects of individual reaction parameters, the following conclusions can be drawn. The mixing in the chamber has double effect. Partly it causes chain scission during or even after the melting of the polymer as a consequence of the shear. Thus, it initiates the degradation mechanically. Partly, it promotes the transport of oxygen into the polymer, thus decreases the diffusion control.

Increase in oxygen concentration promotes completion of oxidation, suppresses crosslinking reactions and formation of unsaturated structures causing yellowish discoloration. It strongly accelerates acid formation. Elevation of temperature increases diffusion control in consequence of different accelerations of chemical reactions and diffusion. It promotes crosslinking in the temperature region studied and hinders formation of functional groups needing much oxygen. Even in systems maximally closed from air, i.e., in a closed mixing chamber simulating processing conditions, considerable changes in molecular mass and in composition can be observed. On the other hand, if aimed, the promotion of the oxygen transport is most important.

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