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CORRELATION BETWEEN OXYGEN UPTAKE AND CARBONYL FORMATION IN POLYETHYLENE OXIDATION

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ABSTRACT

The ratio of absorbed O₂ and carboxyl groups formed was studied in LDPE oxidation. It was found that this ratio is independent of the reaction conditions in a wide range (20–100 kPa O₂ pressure, 90–160°C, and thickness of 20–1170 μm). If the pressure of O₂ was 2.7 kPa, less —COOH formed. A semiempirical mathematic equation was constructed to describe the relation between the acid content and oxygen consumption.

INTRODUCTION

Carboxylic acids are always present among nonvolatile products of polyolefins during oxidation. There is a mutual and unambiguous relation between the amount of acids (*A*) and the total amount of oxygen

consumed (conversion, Z) by the polyethylene (PE) in the oxidation. That relation is independent of oxidation within a wide range, and knowing this relation can make the conceptions concerning the mechanisms of oxidation clearer. The total amount of oxygen consumed (built into the PE + in the volatile products) cannot always be determined directly in the investigation of samples which were oxidized in different ways and conditions. That is the case in the oven aging tests prescribed in the standards. But the amount of carboxylic groups can always be determined in relatively small samples in simple ways [1, 2]. If the relation between the conversion and acid content is known, the conversion can be calculated on the basis of the latter.

The desired mathematical relation can seldom be given in analytical form in a theoretically unobjectionable way because the mechanisms are complicated. For that reason, we wanted to construct a semiempirical form which describes the relation between the relevant concentrations within the error limits of the measurements.

EXPERIMENTAL

Low density PE (Tipolen FA 2210, Tisza Chemical Works, Hungary) was used. Its data and purification have been published [3]. The purified powder was pressed [3] into films of different thicknesses (18–1200 μm), and the films were oxidized in pure O_2 under several constant pressures (2.7, 20, and 100 kPa) and at several constant temperatures (90–160°C) [4]. The acid content of the oxidized samples was measured by titration [1].

RESULTS

The carboxyl content can be seen in Fig. 1 as a function of the total amount of oxygen consumed after oxidation at different temperatures and pressures.

In Figs. 2 and 3 the A vs Z relation is demonstrated for samples of different thicknesses and in the case of oxidation under 2.7 kPa O_2 pressure.

Taking into consideration Figs. 1, 2, and 3, one can conclude that:

1. The trend of curve A vs Z is independent of the O_2 pressure and temperature if the pressure is 20 kPa or higher.

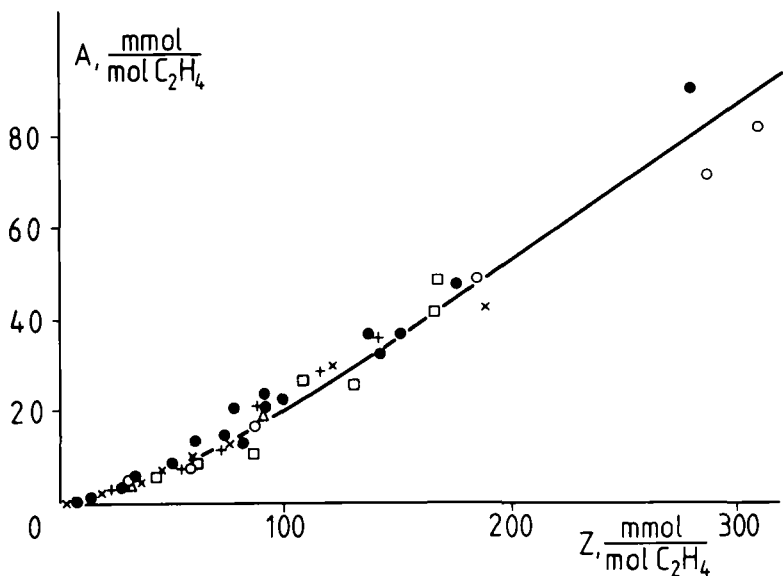


FIG. 1. The carboxyl content (A) of PE films as a function of the total amount of oxygen consumed (conversion, Z). Conditions: pressure, 100 kPa; (Δ) 90°C, (+) 130°C, (\times) 140°C, (\circ) 150°C, (\bullet) 160°C; (\square) pressure, 20 kPa, 140°C; film thickness 20–30 μm in every case. Curve according to Eq. (18) with constants to 20–100 kPa.

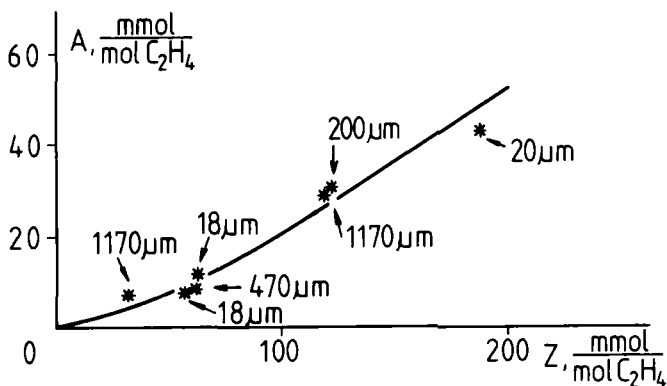


FIG. 2. The carboxyl content (A) of PE films of different thicknesses as a function of conversion (Z). Conditions: 140°C, 100 kPa. The curve is the same as in Fig. 1.

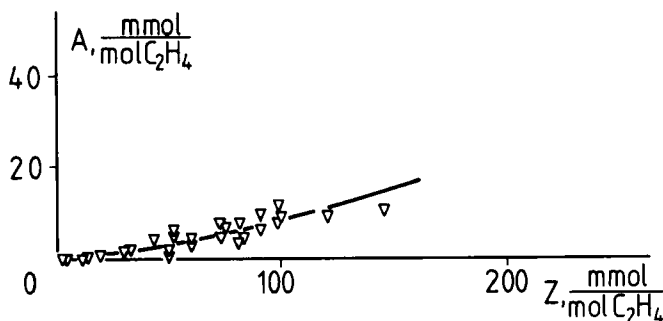


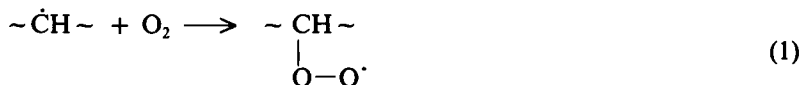
FIG. 3. The carboxyl content (A) of PE films as a function of conversion (Z). Conditions: 150°C , 2.7 kPa , thickness $20\text{--}30\ \mu\text{m}$. Curve according to Eq. (18).

2. The relation between A and Z is independent of the sample thickness at 100 kPa pressure; the curves in Figs. 1 and 2 are the same.
3. The value of A is less after oxidation at 2.7 kPa (20 torr) than it is after oxidation to the same conversion but under higher O_2 pressure.

DISCUSSION

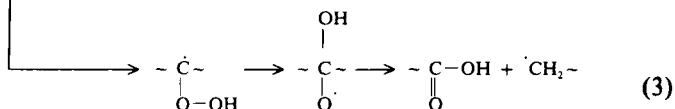
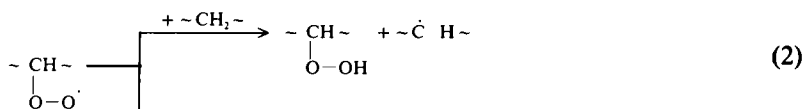
The most important reactions of PE oxidation have been summarized [5]. The mechanisms of the oxidation process will now be surveyed with special respect to the reactions which lead to carboxylic group formation and/or have influence on the relation of A and Z .

In the process of *initiation*, mainly $\sim\dot{\text{C}}\text{H}\sim$ radicals are formed. In *chain propagation* these radicals are oxidized and chain-carrying peroxy radicals are formed:

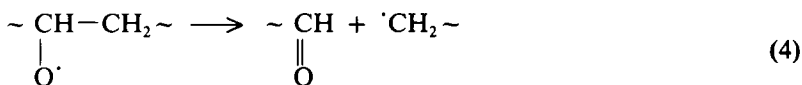


The reaction of peroxy radicals with the substrate results in polymer hydroperoxide formation. On the other hand, part of the peroxy radicals convert directly into carboxylic groups with simultaneous chain scission [6]. Secondary polymeric alkyl radicals are formed in the first pro-

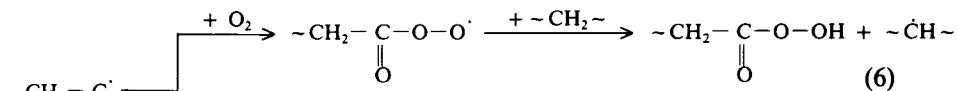
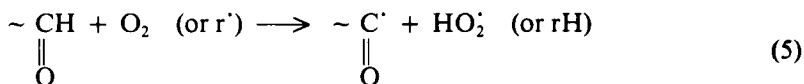
cess and primary polymeric (chain end) alkyl radicals are formed in the second one as chain-carrying radicals:



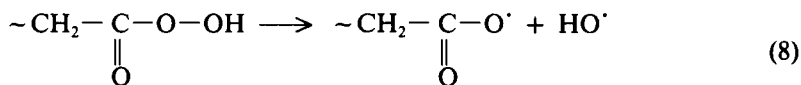
Other authors [7] have also suggested the transformation of peroxy radicals with simultaneous carboxylic group formation in different matrices and under different conditions. About 80% of the polymeric hydroperoxides formed in Reaction (2) change into end products within the cage [5], and a smaller part of the alkoxy and hydroxyl radicals formed can leave the cage and cause chain branching degeneration. The alkoxy radicals formed beside the peroxy radicals are the other precursors of carboxylic acids in PE oxidation:



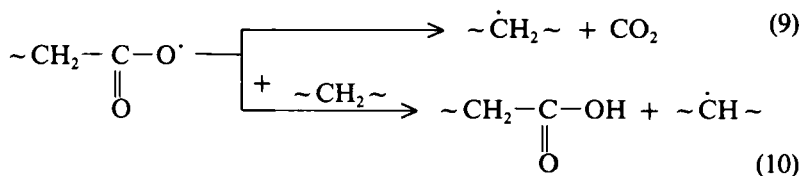
As has been shown [6, 8], aldehydes are also active intermediate products of the process because their oxidation is rapid:



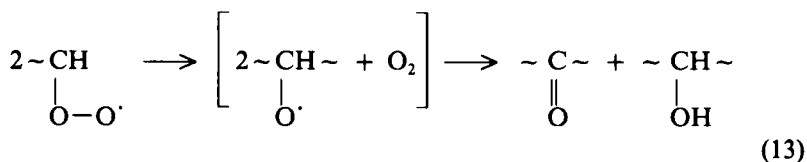
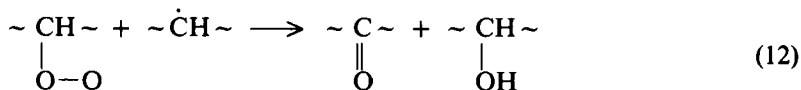
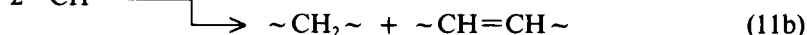
where $r \cdot$ is some kind of radical. Decreasing $[\text{O}_2]$ decelerates Reaction (6). The peracid decomposes while producing radicals (another degenerate chain branching of the process):



The acyl-oxyl radical turns into carboxylic acid, but its decomposition with simultaneous CO₂ formation cannot be ruled out either:

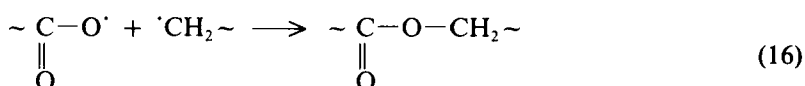
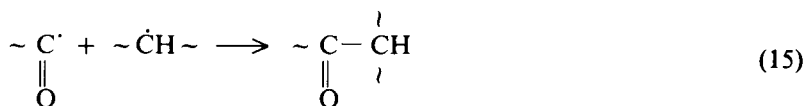
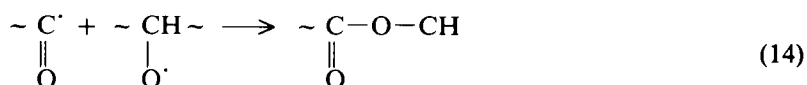


Chain *termination* occurs in the bimolecular homo or cross reaction of the radicals:



If the O₂ pressure is high, termination is mainly the result of Reaction (13), but the role of alkyl radicals increases at low pressure.

One must also take into consideration the termination reactions which decrease the *A/Z* ratio. Some important ones are:



The acyl and acyl-oxyl radicals cannot form carboxylic groups if they take part in Reactions (14), (15), and (16).

The importance of the elementary reactions is shifted if the O_2 pressure changes, which must result in a changed product composition. The IR spectra reflect that fact. In Fig. 4 the spectra of two samples are shown. Both were oxidized to the same conversion, but one at 2.7 kPa O_2 pressure and the other at 100 kPa.

A peak appears at about 1770 cm^{-1} ($\text{C}=\text{O}$ vibration) in the spectrum of PE oxidized under lower pressure, which is only a shoulder in the spectrum of the sample oxidized under 100 kPa O_2 pressure. These facts are evidence for the increased role of Reactions (14)–(16).

The carboxylic groups are formed in two ways according to the unified reaction mechanisms shown above: 1) in the direct isomerization of peroxy radicals (Reaction 3) and 2) in the series of reactions which starts with the radical decomposition of polymeric hydroperoxides (Reactions 4, 6, 8, and 10).

The peroxy radical is the precursor of carboxylic groups in both cases. It is well known that the stationary concentration of peroxy radicals increases with oxygen concentration up to about 20 kPa. At higher $[\text{O}_2]$ their concentration is almost the saturation value. That is why the A vs Z function is independent of the experimental conditions except for very low O_2 pressure (cf. Figs. 1, 2, and 3).

The decomposition of carboxylic groups occurs during oxidation as well. Berezin [9, 10] and Mitskevich [11] detected $^{14}\text{CO}_2$ in the oxidation of a hydrocarbon solution of low molecular weight acids containing $^{14}\text{COOH}$ groups.

Adams [8] suggested that part of the carboxylic acids form esters in polyolefins during oxidation.

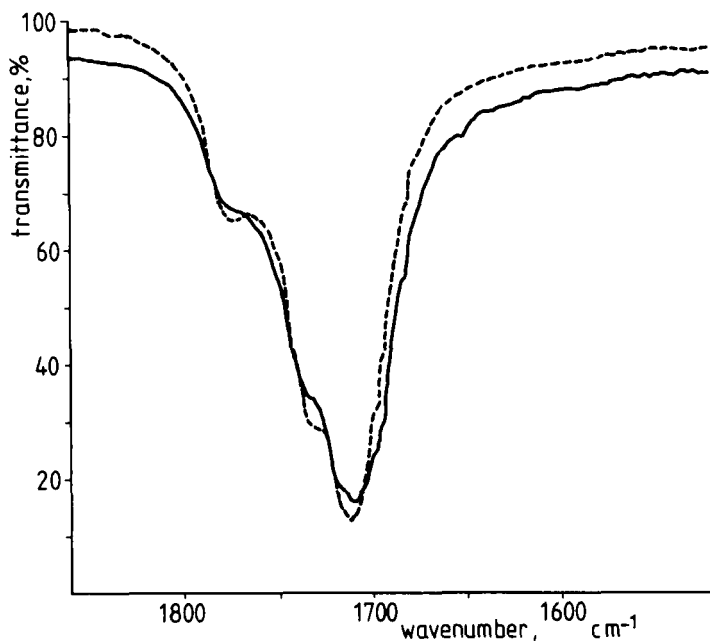


FIG. 4. Part of the IR spectrum of PE films after achieving the conversion of 140 mmol/mol C_2H_4 at $150^\circ C$. Other conditions: 2.7 kPa O_2 pressure, 29 μm thick (dotted line); 100 kPa O_2 pressure, 24 μm thick (solid line).

Although a correct mathematical relation can be found between conversion and acid formation on the basis of the mechanisms shown above, the time-dependent differential equations are rather complicated. Their solution is not possible in an analytical way. For that reason, we tried to construct the desired relation indirectly by using a correlation equation.

Let dZ and dA denote the infinitesimal change of conversion and acid content, respectively. The largest amount of O_2 is consumed in Reaction (1), and we use m_1 as the proportion of peroxy radicals that change into acids in the rapid Reaction (3).

Many radicals and molecules containing oxygen participate in the reaction series (2), (4), (5), (6), (8), and (10), leading to carboxylic group formation. Their total amount is supposed to be proportional to the amount of chemically bound oxygen in PE. The latter is proportional to the conversion, as we have pointed out [12]. If the acid is formed this

way, further O_2 is absorbed in Reactions (5) and (6), and we suppose that this O_2 consumption is proportional to dZ .

The decomposition of carboxylic groups must be correlated with the radicals present in the system, and the rate of oxygen uptake is proportional to the radical concentration. For this reason, we supposed that the amount of decomposing carboxylic groups is proportional to the change of conversion and, on the other hand, to their own concentration:

$$dA/dZ = m_1 + m_2Z - m_3A \quad (17)$$

Upon integration at the initial conditions $Z = 0$ and $A = 0$, we obtain

$$A = (m_2/m_3)Z - (m_2 - m_1m_3)[1 - \exp(-m_3Z)]/m_3^2 \quad (18)$$

The constants of Eq. (18) are given in Table 1.

m_1 could not be determined by using the data concerning the results at 2.7 kPa (its low value had little influence on the residual error during iteration).

The calculation shows that at the beginning of oxidation (where Z is low), the carboxylic groups form mainly in Reaction (3), i.e., during isomerization of peroxy radicals. At pressures of 20 kPa and above, about 5.5% of peroxy radicals change in this way. As the oxidation proceeds, more carboxylic groups form, starting with hydroperoxide decomposition, and the rate of their decay increases as well. This situation develops before the end of the induction period.

The low value of m_1 reflects the fact that the larger part of peroxy

TABLE 1. The Values of the Constants of Equation (18)

Pressure of O_2 , kPa	m_1 , $\frac{\text{mmol COOH}}{\text{mmol } O_2}$	m_2 , $\frac{(\text{mmol COOH})(\text{mol } C_2H_4)}{(\text{mmol } O_2)^2}$	m_3 , $\frac{\text{mol } C_2H_4}{\text{mmol } O_2}$
20–100 ^a	0.0561	5.88×10^{-3}	0.0169
2.7 ^b	2.5×10^{-8}	2.58×10^{-3}	0.0158

^a76 experimental points were used in the calculation.

^b32 experimental points were used in the calculation.

radicals participate in cross-termination with alkyl radicals if the O_2 pressure is low. The value of m_2 is in good agreement with expectation. If the O_2 pressure is high, more hydroperoxides form from the same amount of oxygen absorbed, and there are reactions in the reaction series (2)–(10) which are promoted by higher $[O_2]$ to the detriment of the competing reactions. The value of m_3 does not depend on oxygen pressure. More knowledge concerning the acid decomposition mechanisms is necessary to explain this result.

By having the constants of Eq. (18), one can easily calculate the unknown conversion from the acid concentration if the latter exceeds 10 mmol/mol C_2H_4 . The following approximation can be used:

$$Z = (m_3/m_2)A + (m_2 - m_1m_3)/(m_2m_3) \quad (19)$$

If the acid content is smaller, the curve of Fig. 1 can be used.

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