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Physico-chemical aspects of polyethylene processing in an open mixer. Part 16: Mechanisms and kinetics of ketone formation at low temperature

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Abstract

Ketones are formed essentially on various reactions of polyethylene hydroperoxide. In the low temperature range (150–160 °C), some reactions are the same as in the high temperature range (170–200 °C) of the experiments. However, there is much more complexity at low temperature than at high temperature. The experimental kinetics reveals three significantly different processes compared to only two at high temperature. Ketone formation according to a constant rate results from the cage reaction between a peroxy radical and a hydroperoxide group during the chain propagation reaction. One of the reactions envisaged for the ketones formed according to the rate increasing with processing time in the initial stages is similar from the chemical point of view to the reaction yielding ketones according to the constant rate. The reaction proceeds between the hydroperoxides accumulated in an elementary volume and the peroxy radicals responsible for an additional oxidation of this volume. It cannot be accounted for by formal homogeneous kinetics that accounts well for the constant rate but by the heterogeneous kinetics taking into account repeated oxidation of elementary volumes. The second possibility of ketone formation according to the rate increasing with time is based on bimolecular hydroperoxide decomposition involving mainly associated hydroperoxides. The kinetic treatment for this process combines the heterogeneous kinetics of oxidation volume overlapping with monomolecular decomposition of associated hydroperoxides. The rate constant deduced from the data is in agreement with literature values as well as with the values deduced previously from the experiments with PE melts.
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1. Introduction

Ketones are a major polyethylene (PE) oxidation product in the low temperature range (150–160 °C). Hydroperoxides only are present in larger amount in the early stages of processing [1,2]. Alcohol groups are formed in smaller quantity after significant induction time. Formation of ketones in the high temperature range has been attributed to two main reactions [3]. First of all, ketones are formed in a cage reaction during the propagation step. It involves abstraction of the tertiary hydrogen atom of a secondary hydroperoxide whose formation gave birth to the abstracting radical. Decomposition of the α-hydroperoxy alkyl radical yields a ketone and a hydroxyl radical that is continuing chain propagation. The second major reaction yielding ketones has been attributed to bimolecular hydroperoxide decomposition. The last resulted from direct overlapping of oxidation clusters, i.e. repeated oxidation of the same elementary volume. It can be expected that the

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same mechanisms are operating in the low temperature range. The main difficulty in this respect is that bimolecular hydroperoxide decomposition is no longer fast enough in comparison with the rate of repetitive oxidation of the same elementary volumes. Moreover, several additional mechanisms must be envisaged for the low temperature range. The last is characterized by a rate of ketone formation increasing during the time period of the experiments. This constitutes a significant difference with the high temperature range where this rate becomes rapidly constant.

2. Experimental

Additive free low-density polyethylene (PE-LD, density = 0.918, melt flow (190 °C/2.16 kg) = 0.3) was plasticized for various times in a Brabender-plastograph open to air, at different temperatures and 30 rpm. The polymer oxidized this way to different extents was taken out of the mixer and cooled immediately in a cold press. This material was used to prepare films of the desired thickness by compression molding under mild conditions to minimize hydroperoxide decomposition. Typically, it was performed at 150 °C for 2 min. The films up to 0.5-mm thickness were immediately quenched in cold water (10 °C). The 1-mm thick plaques were not quenched in water but cooled in a cold press with circulating water.

Functional group formation was measured by IR spectrophotometry with an untreated sample in the reference beam. The spectrophotometer used was a Perkin—Elmer FT-IR 1710. The hydroperoxide concentrations are expressed by the absorbance of the free (E_{3552}) and associated hydroperoxide groups (E_{3410}) absorbing at 3552 and 3410 cm^{-1}, respectively. All the values have been adjusted to a sample thickness of 1 mm. It has been found that, with the PE-LD used in the experiments, melt temperature exceeded nominal temperature by 10 °C [2].

This means that the nominal temperature of 150 °C, e.g., corresponded to a melt temperature of 160 °C. Recent experiments have shown that this is true for approximately 1 h processing in the low temperature range. Afterwards, the temperature is decreasing slowly. The decrease corresponds to a loss of approximately 4—5 °C after 4 h processing so that after that time the melt temperature was 155—156 °C instead of the nominal 150 °C. The experimental results will be given for the nominal temperature. However, whenever the effect of temperature is being examined, the real melt temperature will be taken into account.

The knowledge of the approximate extinction coefficients of the different functional groups is mandatory for comparison purposes. For free and associated hydroperoxides, a value of 90 seems reasonable [2].

The values found with primary and secondary alcohols in solid PE-LD are in the range of 40—50 [2]. Hence, a factor 2 between the extinction coefficients of alcohol and hydroperoxide groups seems accurate enough. Similarly, the extinction coefficient of ketones is about 360 [4] i.e. a factor 4 in comparison with hydroperoxides.

3. Review of the kinetics

3.1. Elementary experimental kinetics for ketones

Ketone formation in a mixer open to air can be expressed by an equation [2,3] containing a linear and a quadratic term in processing time as it is shown in Eq. (1):

$$(PE=O) = R_1 t + R_2 t^2 \tag{1}$$

with the parameters R_1 and R_2 depending on the polymer and the processing conditions. If Eq. (1) accounted really for the experimental results as it seems implied by the good fit of the data, the plot of the ketone absorbance divided by the corresponding processing time, as a function of this processing time should yield one straight line. However, most often this is not so and the data can be accounted for by two different segments of straight lines.

Nevertheless, in spite of lacking direct physical meaning, the representation of the ratio of the concentration to the processing time as a function of this processing time proves to be very useful for data interpretation. Fig. 1 shows a typical plot valid for the ketones in the low temperature range. The first segment
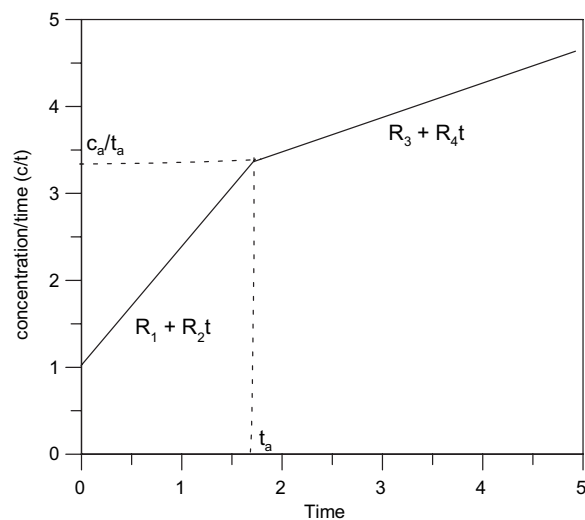

Fig. 1. Schematic representation of the variation of the ketone concentration divided by the processing time as a function of this processing time. Arbitrary units.