Co-oxidation kinetic model for the thermal oxidation of polyethylene-unsaturated substrate systems

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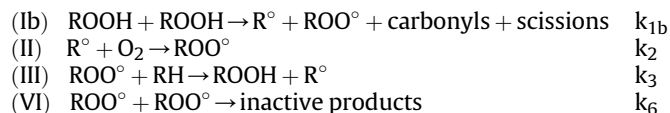
ABSTRACT

The thermal oxidation of polyethylene (PE) impregnated by the methyl esters of unsaturated fatty acids (UFEs) was studied using chemiluminescence, and infra-red spectrophotometry. It was shown that the presence of UFEs accelerates the PE aging process. This can be interpreted as a co-oxidation phenomenon. In this study, the previously established models for PE and UFEs self-oxidation have been coupled in order to develop a co-oxidation model. Using the existing rate constants for the PE and UFEs self-oxidations, this model can simulate the complex shape of the kinetic curves of PE-UFE co-oxidation.

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1. Introduction

In a first approach, the oxidation mechanism at relatively moderate temperatures ($<150\,^\circ$C) of a hydrocarbon substrate with a single reactive site, when there is an oxygen excess (that is when there is no contribution of alkyl radicals P° to the termination reactions) can be depicted by the following scheme [1,2]:

(Ib) $ROOH + ROOH \rightarrow R^\circ + ROO^\circ + \text{carbonyls} + \text{scissions}$ k_{1b}
(II) $R^\circ + O_2 \rightarrow ROO^\circ$ k_2
(III) $ROO^\circ + RH \rightarrow ROOH + R^\circ$ k_3
(VI) $ROO^\circ + ROO^\circ \rightarrow \text{inactive products}$ k_6

Over the years, this model as well as several completed versions has been developed with a view to describing the oxidation of substrates under specific reaction conditions, namely, when it can be assumed that there is only one kind of reactive site which corresponds to the weakest C–H bond and the highest propagation rate constant k_3 [3]. Some examples are: tertiary carbons in polypropylene [4], secondary carbons in polyethylene [5] and allylic ones in butadiene rubber [6].

It is well documented that oxidation can be favored by metallic impurities playing a catalytic (redox) role [7] or by species such as carboxylic acids capable of establishing strong hydrogen bonds with the polymeric ROOH groups [8]. These cases of assisted oxidation differ from the co-oxidation phenomena described in this current study. Here, the simultaneous in chain oxidation of two different kinds of reactive sites corresponding to two categories of C–H groups will be studied.
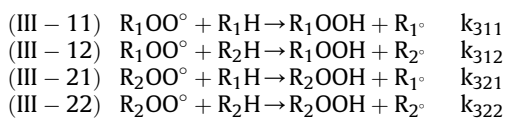
In such a case of co-oxidation, Decker et al. [9] showed that the oxidizability of ethylene propylene copolymer varies with the ethylene molar fraction e according to a pseudo-hyperbolic curve which can be approximated by the following function:

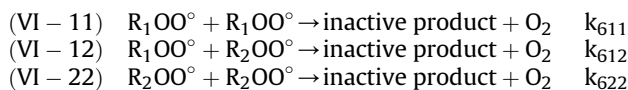$$\frac{k_3}{\sqrt{k_6}} = 10^{-4} \times \frac{2 - 1.63 \times e}{1 + 3.13 \times e}$$

here k_3 and k_6 can be defined as the rate constants characteristic of a virtual homopolymer which would exhibit the same kinetic behavior as the copolymer under study. In fact, an approach in which the kinetic behavior of the copolymer could be predicted from the characteristics of the corresponding homopolymers would be far more satisfactory. In the case of propagation, the presence of two reactive sites needs to take into account four elementary reactions:

(III − 11) $R_1OO^\circ + R_1H \rightarrow R_1OOH + R_{1^\circ}$ k_{311}
(III − 12) $R_1OO^\circ + R_2H \rightarrow R_1OOH + R_{2^\circ}$ k_{312}
(III − 21) $R_2OO^\circ + R_1H \rightarrow R_2OOH + R_{1^\circ}$ k_{321}
(III − 22) $R_2OO^\circ + R_2H \rightarrow R_2OOH + R_{2^\circ}$ k_{322}

In the case of termination, one cross termination must be added to the two self-terminations:

(VI − 11) $R_1OO^\circ + R_1OO^\circ \rightarrow$ inactive product $+ O_2$ k_{611}
(VI − 12) $R_1OO^\circ + R_2OO^\circ \rightarrow$ inactive product $+ O_2$ k_{612}
(VI − 22) $R_2OO^\circ + R_2OO^\circ \rightarrow$ inactive product $+ O_2$ k_{622}

Russell [10] proposed the following expression for the oxidation rate:

$$r_{OX} = \frac{\frac{k_{311}}{k_{322}}[R_1H]^2 + 2[R_1H][R_2H] + \frac{k_{322}}{k_{321}}[R_2H]^2}{\sqrt{\frac{2k_{611}}{k_{312}^2}[R_1H]^2 + \frac{2k_{612}}{k_{321} \cdot k_{321}} \cdot [R_1H][R_2H] + \frac{2k_{622}}{k_{321}^2}[R_2H]^2}} \cdot \sqrt{r_i}$$

In it he assumed an unique initiation reaction of constant rate r_i, a steady state and long kinetic chains. Apart from those two pioneering works, little has been done on co-oxidation mechanisms either from the experimental [11] or from a modeling approach [12]. This is in spite of the fact that solving the complex differential systems derived from the co-oxidation scheme is nowadays relatively easy thanks to numerical solvers.

In this paper, we introduce a co-oxidation model for PE + the methyl esters of unsaturated fatty acids (UFEs) from vegetable sources. There is a need for such a model because:

- UFEs are the main components of biodiesels obtained from vegetable sources. Since these will come into contact with the polyethylene parts of automotive engines such as tanks [13] (if they are not protected by physical barriers such as fluorinated polymers). The question arises do the UFEs interact with the PE oxidative aging process to the detriment of the polymer durability? This problem, which is becoming increasingly important, has received little attention until now.
- From a theoretical point of view, the UFEs system appears interesting owing to the clear difference in the oxidizabilities of PE and the UFEs it can be impregnated with (holding either 1, 2 or 3 double bonds). The oxidation of each individual substrate PE, methyl oleate, methyl linoleate and methyl linolenate) have all been previously studied [5,14]. Hence, PE + UFE mixtures are ideal systems for the study of co-oxidation kinetics.

One criticism regarding the development of a possible kinetic model is the elevated number of rate constants being *a priori* adjustable parameters permitting to fit any experimental results. Here, any model proposed should meet three requirements:

① It must simulate the relatively most complex shape of the co-oxidation curves for processes involving two substrates with different reactivities.
② It must involve kinetic parameters identical to those determined for modeling the oxidation of the pure polyethylene [5] as well as the pure methyl esters [14].
③ Its heuristic properties should permit it to predict the relative contribution of each substrate to the global oxidation curves monitored by FTIR or chemiluminescence.

With this in mind, the coupled degradation of a PE-UFE series was studied using chemiluminescence at 150 °C. Another solid state (80 °C) series was also studied in an effort to separate the PE and UFEs oxidation by-products.

2. Experimental

2.1. Materials

Polyethylene was supplied as an antioxidant free powder. This was verified by observing the absence of an induction period at 200 °C. DSC analysis revealed a melting temperature of 132 °C with a melting enthalpy close to 150 J g^{-1}. This corresponds to a crystallinity ratio of about 50%.

According to Demirbaş et al. [15], vegetable oils are mainly composed of the methyl esters of fatty acids with 16 or 18 carbons in their linear hydrocarbon chains. Two important compounds are methyl oleate and methyl linolenate which have different oxidative stabilities. Methyl oleate (ref S54470-478) and methyl linolenate (ref 62210) were supplied by Sigma Aldrich.

The impregnation of the methyl esters into the PE at various temperatures has been previously described [16]. To summarize the initial state of the materials used were: ① pure PE, ② PE impregnated with 5% weight methyl oleate, ③ PE impregnated with 10% weight methyl oleate and ④ PE impregnated with 5% methyl linolenate.

2.2. Exposure conditions

Impregnated films were submitted to one of the two following conditions: ① thermal aging in ovens at 80 °C monitored by FTIR, ② thermal aging at 150 °C under 0.1 MPa O$_2$ monitored *in situ* by CL.

2.3. Characterization

2.3.1. Chemiluminescence
Chemiluminescence experiments were performed using a Lumipol 3 apparatus designed in-house at the Polymer Institute in the Slovak Academy of Sciences [7]. Films impregnated by methyl oleate and linolenate were placed into aluminum pans and heated under nitrogen to 150 °C. They were then maintained at this temperature under oxygen at 0.1 MPa pressure.

2.3.2. Extraction of the methyl esters of the unsaturated fatty acids
After thermal oxidation of the PE impregnated by UFE, both the UFE and its oxidation by-products were extracted using CH$_2$Cl$_2$ overnight at room temperature. An example of the observed differences in the FTIR spectra between an impregnated PE sample both before and after extraction are shown in the spectra in Fig. 1 at $t = 0$. These show the total UFE extraction. Those in Fig. 3 represent the samples after several exposure durations.

2.3.3. FTIR
FTIR spectra of the PE films were recorded in transmittance mode using a Spectrum 100 spectrophotometer (Perkin Elmer), with 4 scans at 4 cm^{-1} resolution. Both the virgin and oxidized methyl esters of the unsaturated fatty acids display an absorption peak at ca 1740 cm^{-1}. After removing the UFEs and its soluble by-products from PE, only a peak at 1720 cm^{-1} remains. This is attributed to carbonyl compounds resulting from the PE oxidation. The carbonyl absorbance before and after extraction were converted into concentrations using the molar absorptivity of 300 l mol^{-1} cm^{-1} [17].