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# Kinetic modelling of the thermal oxidation of polyisoprene elastomers. Part 2: Effect of sulfur vulcanization on mass changes and thickness distribution of oxidation products during thermal oxidation

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## Abstract

Thermal oxidation of sulfur vulcanized polyisoprene samples was studied by gravimetry and IR mapping of carbonyl groups (to determine the oxidized layer thickness (TOL)) at temperatures ranging from 60 to 150 °C in air. Oxidation appears noticeably lower than that for the starting non-vulcanized polyisoprene, revealing a stabilizing effect of sulfur-containing species. After a short period where mass loss presumably due to water evaporation predominates, the sample mass increases until a plateau corresponding to 6.3% (at 60 °C) to 0.5% (at 140 °C) mass gain. Practically no weight gain (∼0.1%) was observed at 150 °C. The mass uptake is due to oxygen grafting to the chains. TOL varies from about 4.6 mm (70 °C) to about 1 mm (150 °C).

A kinetic model, derived from a mechanistic scheme of radical chain oxidation including stabilizing events due to hydroperoxide reduction by sulfur-containing groups and taking into account the diffusion–reaction coupling, was established and numerically resolved. The model predictions for mass changes and TOL values are in good agreement with experimental data.
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## 1. Introduction

The thermal oxidation of polyisoprene and natural rubber elastomers has given rise to an impressive amount of scientific literature in the past century. Despite that, one of the main objectives of this research, i.e. the elaboration of a non-empirical model for lifetime prediction, was never reached. Among the multiple reasons of this failure, the following are obvious: the high complexity of oxidation mechanisms, the extreme difficulty of determining certain elementary rate constants and the lack of analytical solutions for the kinetic schemes.

What is new today is that powerful computer tools are available for solving complicated kinetic schemes. This opens the way to the determination of elementary rate constants using inverse approaches [1,2]. It thus becomes possible to overcome obstacles which, in the recent past, were considered insuperable. In the case of vulcanized and stabilized polydiene elastomers, the complexity of kinetic schemes (more than 30 parameters) forces us to have a graduated approach. The first step [1] was aimed at determining the kinetic parameters characterizing the oxidation of non-vulcanized and non-stabilized polyisoprene. It remains now to determine parameters relative to the vulcanizing and stabilizing systems. Concerning the effects of vulcanization, it appeared necessary to distinguish two parts: the effect of vulcanization on the overall oxidation rate and the effect of oxidation on the network structure,

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particular attention being paid to vulcanizing species. The present article deals with the first part, i.e. the effect of vulcanization on the oxidation kinetics. It has been chosen, here, to study a semi-efficient sulfur vulcanization.

A relatively abundant literature exists on thermal ageing of sulfur vulcanized natural rubber or polyisoprene (SVPI). Unfortunately, most published work concerns the consequences of thermal ageing on mechanical properties, which will be the subject of the next part of this article. However, it is practically useless understanding the role of sulfur vulcanization on oxidation kinetics. As a matter of fact, mechanical properties changes can be also induced by anaerobic processes independent of the radical chain oxidation. Oxygen absorption measurements are in principle well adapted to structure—oxidizability studies. This method was used, for instance, by Dufraisse and Etienne to show that oxidizability increases with the content of combined sulfur [3]. Certain studies reviewed for instance by Bevilacqua [4] reached opposite conclusions, whereas others find a non-monotonic dependence of oxidation rate on the sulfur content [5]. These discrepancies can be explained, at least partially, by the complexity of sulfur vulcanizates in which one can distinguish the free and reacted sulfurs, the latter being present in a wide variety of structures such as heterocycles, mono- and polysulfide bridges, etc. [6—8]. They are, at least partially, in equilibrium with unreacted sulfur. Early studies reported an antioxidant effect of certain sulfur-containing groups. For Degteva and Kuzminskii [9], it could be due to the sulfur liberated by the decomposition of polysulfinic bridges, but Bateman et al. [10,11] demonstrated, using model compounds, that alkyl sulfides could display a stabilizing role through hydroperoxide decomposition. Disulfide can also react with hydroperoxides, but the corresponding stabilizing effect could be compensated by the decomposition of the resulting sulfoxide leading to selective crosslink destruction [12].

Finally, the fact that the vulcanizate's oxidizability depends on a wide variety of parameters characterizing the vulcanization system makes a coherent synthesis of literature data difficult. A kinetic model taking into account all this complexity is out of reach at this state of our knowledge. Nevertheless, it seemed to us interesting to build a simplified model in which the vulcanization effect on oxidation would be represented by a small number of elementary processes chosen in order to predict the main trends of oxidation kinetics. This part is essentially focused on the elaboration of the model. It has been chosen to work on bulk samples, i.e. to take into account the kinetic control of oxidation by oxygen diffusion that complicates the model, but offers an interesting way of validation by experimental determination of oxidation thickness profiles. Another step of validation could be accomplished in the next part of this article, where the ability of the model to predict ageing-induced mechanical property changes will be tested.

## 2. Experimental

The experiments were conducted on an unstabilized SVPI prepared by LRCCP from a commercial linear polyisoprene of predominantly *trans* 1,4 structure: Natsyn 2200

($\rho = 921$ kg m$^{-3}$ and $M_{W0} \approx 2500$ kg mol$^{-1}$) provided by Goodyear.

The composition of the starting mixture is (in parts by weight) Natsyn 2200 (100 parts), stearic acid (2 parts), zinc oxide (5 parts), sulfur (1.5 parts) and CBS (*N*-cyclohexyl-2-benzothiazolesulfenamide, 1.5 parts). It has been chosen, here, to study a semi-efficient sulfur vulcanization.

The mixture was homogenized at 70 °C during 23 min in an open mixer. During this stage, the average molecular mass of the Natsyn 2200 decreases to $M_{W0} \approx 1800$ kg mol$^{-1}$.

Two types of SVPI samples were processed by press moulding: films of thickness ranging between 0.2 mm and 0.7 mm and plates of thickness ranging between 2 mm and 70 mm. The vulcanization conditions of the plates are 35 min and 90 min at 150 °C for, respectively, 2 mm and 70 mm thickness.

SVPI films were placed between two chambers: the first one contains pure oxygen at 2 bar pressure whereas the second one is initially in air under atmospheric pressure (1 bar), in order to determine the oxygen permeability coefficients $P_e$ at various temperatures ranging from 50 to 90 °C. The gas penetrating into the second chamber induces an increase of the pressure which is recorded. Oxygen permeability coefficients $P_e$ were determined according to ISO 2782:1995 at constant volume.

Rectangular bulk specimens were exposed to air between 60 and 150 °C in ventilated ovens, regulated at ±1 °C, and removed from ovens at definite times for physico-chemical analysis.

Some samples were examined by IR spectrophotometry after microtome cutting of slices perpendicular to sample surfaces. The slices were analyzed by a Bruker IFS 28 IR spectrophotometer, with a minimal resolution of 4 cm$^{-1}$, in transmission mode in the region of 1710—1740 cm$^{-1}$ in order to determine the thickness distribution of carbonyl groups from the free surface to the specimen core (FTIR mapping).

Other samples were periodically removed from ovens and cooled to room temperature in a desiccator before being weighed using a Mettler Toledo AT 261 microbalance with a sensitivity of 10$^{-4}$ g. After weighing, these specimens were returned to the ovens.

## 3. Results

### 3.1. Oxygen permeability coefficients

Oxygen permeability coefficients $P_e$ determined between 50 and 90 °C are listed in Table 1.

$P_e$ obeys Arrhenius law:

$$P_e = P_{e0} \exp\left(-\frac{E_{Pe}}{RT}\right) \tag{1}$$

where $P_{e0} = 6.3 \times 10^{-12}$ m$^3$ (STP) m$^{-1}$ Pa$^{-1}$ s$^{-1}$ and $E_{Pe} = 25.5$ kJ mol$^{-1}$.