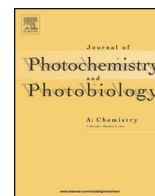




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A general kinetic model for the photothermal oxidation of polypropylene

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ABSTRACT

A general kinetic model for the photothermal oxidation of polypropylene has been derived from the basic auto-oxidation mechanistic scheme in which the main sources of radicals are the thermolysis and photolysis of the most unstable species, i.e. hydroperoxides. Thermolysis is a uni- or bi-molecular reaction whose rate constant obeys an Arrhenius law. In contrast, photolysis is exclusively a unimolecular reaction and its rate constant is independent of temperature. According to the quantum theory, this latter is proportional to the energy absorbed by photosensitive species and thus, accounts for the impact of UV-light intensity and wavelength on the global oxidation kinetics.

The validity of this model has been checked on iPP films homogeneously oxidized in air over a wide range of temperatures and UV-light sources. It gives access to the concentration changes of: (i) primary (hydroperoxides) and secondary (carbonyls) oxidation products, (ii) double bonds, (iii) chain scissions and crosslinking nodes, but also to the subsequent changes in molecular masses. These calculations are in full agreement with the photolysis results reported by Carlsson and Wiles in the 70s [1–3]. However, the model seems to be only valid for UV-light energies equivalent to about 10 suns as upper boundary, presumably because of multiphotonic excitations or chromophores photosensitization (i.e. termolecular photo-physical reactions), both enhanced at high irradiances.

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1. Introduction

There is an increasing demand of automotive industry for the development of numerical calculation tools allowing to criticize and enhance the representativeness of accelerated aging testing methodologies and to predict the lifetime of polymer parts. In this perspective, non-empirical kinetic approaches appear to be most relevant since they would capitalize knowledge. The first attempts to model the oxidation kinetics of hydrocarbon polymeric substrates were done by Tobolsky et al. [4,5] with the perspective of predicting their long-term behavior. Their analytical model was derived from an oversimplified mechanistic scheme in which the radical chain oxidation was composed of only four elementary chemical steps. Initiation consisted in the formation of radical species either from the thermal decomposition of hydroperoxides or from the effect of extrinsic factors (e.g. a radiation source).

Propagation took place in two successive stages: the rapid addition of oxygen onto alkyl radicals followed by the slower hydrogen abstraction on polymer substrate by peroxy radicals. Finally, termination consisted only in the bimolecular combination of peroxy radicals. Thus, according to these authors, thermal and photochemical oxidation could be described by a very close mechanistic scheme differing only by their initiation step. A mathematical expression for oxidation rate was obtained through the conventional concepts of chemical kinetics by making four simplifying assumptions: (1) unicity of reactive site, i.e. oxidation occurs exclusively on the most labile CH bond; (2) low conversion ratios of oxidation process, i.e. concentration of reactive sites remains virtually constant; (3) constancy of initiation rate in the case of oxidation induced by an extrinsic factor; (4) and steady-state for radicals concentrations in all oxidation cases, but also for hydroperoxides concentration in the case of pure thermal oxidation. This kinetic modeling approach turned out to be astonishingly efficient despite its apparent simplicity. It allowed predicting accurately the homogeneous thermo-, photo- and radio-oxidation of thin polymer films (typically 100 μm thick)

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exposed under a sufficiently high oxygen partial pressure to fully saturate the sample in oxygen, i.e. to reach the so-called regime of oxygen excess.

Kinetic developments were then made by Bolland and Gee [6], Reich and Stivala [7,8], Cunliffe and Furneaux [9,10] and Audouin et al. [11], but also by Gillen et al. [12], with the objective to describe other oxidation regimes of lower oxygen concentration than oxygen excess. These authors added other possible termination reactions, namely bimolecular combinations of alkyl-alkyl and alkyl-peroxy radicals, to the previous mechanistic scheme. They obtained a hyperbolic expression for oxidation rate by making two additional simplifying assumptions (in addition to the previous four assumptions): (5) long kinetic chain; (6) and existence of an interrelationship between termination rate constants. This model allowed to describe the oxygen concentration dependence of the oxidation rate of thin polymer films and to determine the critical value of the oxygen partial pressure above which oxygen is in excess. Moreover, when coupled with the Fick's second law (for oxygen diffusion) into an oxygen balance equation, this model allowed also to accurately predict the concentration profiles of oxygen and oxidation products in thick polymer samples (typically few mm thick).

Since then, new kinetic developments were made by Gillen et al. [12] and Colin et al. [13,14] to reduce the number of questionable simplifying assumptions and thus, increase the robustness of the analytical kinetic model.

In the eighties, the advances of the previous decades in the elucidation of chain radical oxidation reactions and the emergence of new numerical algorithms especially adapted for solving stiff problems of chemical kinetics, enabled Sommersal and Guillet to envisage the development of a numerical model for polyolefins photooxidation [15]. Their approach consisted in considering all the possible elementary chemical steps (up to sixty) and assigning them a rate constant whose value was determined on model compounds, when possible. Such an exhaustive approach was very attractive since it enabled to eradicate all the questionable simplifying assumptions (except assumption 1), but it failed because the numerical problem to be solved was largely oversized. Indeed, for most oxidation cases, too many rate constants were unknown and some of them were experimentally out-of-reach.

This observation encouraged our research team to propose an alternative approach of kinetic modeling. It consists in deriving a kinetic model from a simplified, but realistic, oxidation mechanistic scheme by focusing on the critical oxidation path, i.e. constituted of the main contributory reactions to photothermal oxidation. In the case of pure thermal oxidation, it is called the "closed-loop mechanistic scheme" (CLMS) [16–18], since, the main source of radicals is the thermal decomposition of its main propagation products, i.e. hydroperoxides.

In the early 2000s, this numerical tool has been extended to solve oxidation problems initiated by extrinsic species or factors, in particular gamma-irradiation in a nuclear environment [19]. Now, it remains to extent this approach to the case of photothermal oxidation. However, the quantitative impact of UV-light on the initiation step of oxidation has not been clearly formalized. The introduction of a term of photo-induced initiation in a numerical model has been performed by Kiil in the case of the photooxidation of epoxy coatings, but the corresponding initiation rate has been described through an empirical law [20], whereas it would be possible to use the quantum theory. A criterion, based on the absorbed energy by photosensitive species, was recently proposed in this purpose and tested through an analytical model [21]. This theory allowed describing the competition between thermal and photochemical initiations during polypropylene oxidation. However, the analytical treatment prevented from introducing photochemical initiation by multiple photosensitive species, and

the values of quantum yields were excessive compared with the experimental values reported by Carlsson and Wiles [1–3,22].

The objective of the present publication is to extend the numerical kinetic model, beforehand established for pure thermal oxidation, to the photothermal oxidation of isotactic polypropylene (iPP) by taking into account the additional effect of UV-light sources. After having checked its validity, this model will be used for investigating the relative predominance of two important photosensitive species (namely peroxide type species and ketones) in the initiation step of photothermal oxidation which, still today, remains a controversial topic in the literature.

2. Experimental part

2.1. Materials

The iPP under investigation was supplied as pellets by Aldrich (under the reference 427,888). Its main physico-chemical characteristics are: MFI [230 °C, 216 kg] = 12 g/10 min, $M_w = 250 \text{ kg mol}^{-1}$, $M_n = 67 \text{ kg mol}^{-1}$ and $PI = 3.7$. Films of 80–135 μm thick were processed by compression molding in a Gibitre laboratory press during 1 min at 200 °C under 20 MPa, and then purified from their stabilizers by Soxhlet extraction for 48 h using dichloromethane as solvent prior to aging experiments.

2.2. Photothermal aging

In order to decouple UV-light from thermal effects, iPP films were exposed under different light intensities and temperatures, always in dry conditions. Photothermal aging experiments were mostly performed on films of 80 μm thick in a series of SEPAP devices equipped with 80 W medium pressure arc mercury lamps having a borosilicate filter. To vary the light intensity, the number of lamps was changed from 2 to 4 lamps in a SEPAP 12-24 device, and from 6 to 8 lamps in a SEPAP 50-24 device. Both light intensity and emission spectrum were measured using a IL390C radiometer in the 295–415 nm range and a Avantes spectro-radiometer (AvaSpec 2048 \times 14-USB2, 0.7 nm resolution) in the 250–750 nm range respectively. Temperature was fixed at 45, 60 or 80 °C according to the apparatus specifications and directly monitored on sample surfaces using a thermo-button temperature logger. A photothermal aging test was also performed on films of 135 μm thick in a WeatherO'Meter device (WOM) equipped with a xenon lamp and borosilicate S/S filters. The black (BPT) and white standard (WST, i.e. chamber) temperatures were fixed at 70 and 55 °C respectively. The temperature of the sample was found to be intermediary at 64 °C, whereas the irradiance at 340 nm was measured at $0.46 \text{ W m}^{-2} \text{ nm}^{-1}$, without water spraying. The thermal oxidation (in the absence of UV-light) was also investigated in air-ventilated ovens for temperatures ranging from 60 to 140 °C.

To ensure the test reproducibility (between samples stemming from different batches during their purification from stabilizers) and to determine a sampling frequency suitable for an accurate description of the oxidation kinetics (particularly fast under the harsher aging conditions), it was decided to proceed in two stages:

- A non-destructive monitoring of carbonyl oxidation products by FTIR spectrophotometry, repeated for all aging conditions on samples coming from three different batches.
- Both destructive (hydroperoxide titration, gel permeation chromatography, DSC, etc.) and non-destructive analyses (FTIR spectrophotometry) on samples from different batches, periodically removed from the aging devices.

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