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Molecular and macromolecular structure changes in polyamide 11 during thermal oxidation

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ABSTRACT

The present article reports a study of thermal oxidation of unstabilized polyamide 11 films at several temperatures (90–165 °C) under atmospheric pressure and under various oxygen pressures (up to 1.6 MPa) at 110 °C. The chemical structure changes are monitored by IR spectroscopy (carbonyl groups) and UV–visible spectrophotometry (yellowing). Molar mass changes are determined by size exclusion chromatography (SEC). By investigating the influence of oxygen pressure it is clearly shown that reactions involving P° radicals other than O_2 addition cannot be neglected under atmospheric pressure. Under the conditions of this study limited to relatively low oxidation levels, IR and UV measurements indicate that carbonyl groups and chromophores responsible for yellowing have the same relative yield whatever the temperature and oxygen pressure. SEC measurements highlight the significant predominance of random chain scissions over crosslinking events. Crosslinking only appears after an induction time, presumably because it involves reactions between primary oxidation products. The ratio of carbonyl groups over chain scissions is about 7.5 at low conversion and about 2.5 at high conversion, showing that α amino alkoxy radicals are mainly transformed into imides without chain scission.

1. Introduction

Polyamides are reactive with oxygen and undergo thermal oxidative degradation even at moderate temperature. In practice, oxidation results in the deterioration of optical and mechanical properties. Since lifetime prediction is essential for polyamide users and producers, this work is aimed at elaborating a model based on a non-empirical kinetic scheme for predicting the time to embrittlement in given exposure condition. This article reports the first step of the kinetic approach which is the choice of reliable input data to the model and the prediction of the degree of yellowing and the molar mass value, this latter being linked to mechanical properties.

Practically, all the authors having studied polyamide thermal oxidation and model compounds have elaborated mechanisms starting from the hypothesis that oxidation is a radical chain mechanism mainly propagated by hydrogen abstraction on α-*N*-methylene. This selectivity is supported by experimental and thermochemical arguments [1,2]. Many authors assume implicitly or explicitly that the process is 100% selective that would be surprising for a radical process. In fact, little is known on the selectivity degree of this propagation mechanism. Considering in a first approach that: i) H abstraction is 100% selective and ii) 100% of initiation events result from α-*N*-hydroperoxide decomposition, it is possible to formulate the mechanistic scheme of Fig. 1.

Fig. 1 schematizes polyamide oxidation which is shown to have common characteristics with liquid hydrocarbon or polyolefins i.e. a closed loop behavior: radicals are generated from POOH decomposition (possibly by a unimolecular process) and propagate to yield to another POOH. Several reactions (terminations, pathways from POOH to P°) are not shown in the aim of simplicity.

In a recent review, we analyzed data from literature using kinetic analysis in order to assess reliable values of kinetic parameters [3]. However, we faced several contradictions:

- According to El-Mazry et al. [4], the ratio between chain scissions and carbonyls would be close to unity, contrary to the experimental observation by Sagar [5] and later Lemaire et al. [6] according to which imides are the main oxidation product. Since imides are formed without chain scission, the ratio of

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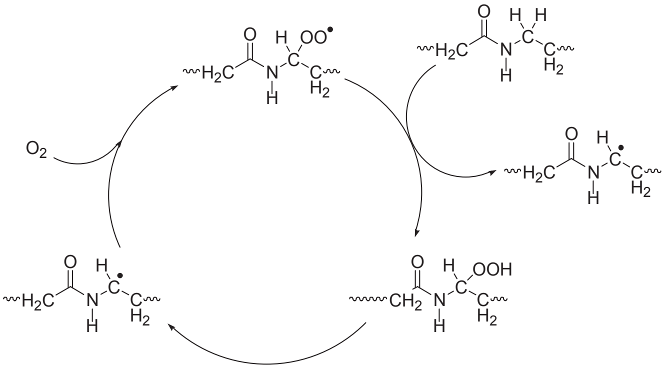

Fig. 1. Closed loop behavior of polyamide 11 oxidation.

chain scission/carbonyl would be expected significantly lower than 1.

- In our attempts to simulate existing kinetic curves from oxygen uptake or carbonyl build-up in air [3], we applied an extremely high rate constant value for the termination reaction (6) involving two peroxy radicals:

(6) $\mathrm{POO^\circ + POO^\circ \rightarrow}$ inactive products

However, how can we ensure the real value of this constant has been correctly assessed? An overestimation is likely to happen since we neglected other termination processes such as:

(4) $\mathrm{P^\circ + P^\circ \rightarrow}$ inactive products

(5) $\mathrm{P^\circ + POO^\circ \rightarrow}$ inactive products

Both processes are expected to have higher rate constants than the one associated to (6) [7,8].

In the present study, new data are brought in order to discuss the previous questions:

- Aging experiments under several oxygen pressures are performed in order to get accurate values for termination rate constants [7],
- A special attention is paid to molar mass distribution changes determined by size exclusion chromatography (SEC). The latter technique [9,10] appears to be relevant in comparison with rheometry measurements [4] where part of the oxidized polymer may undergo thermolysis as the measurements are performed in molten state. Furthermore, SEC is expected to be more informative than viscosimetry (only M_W [11]) with the aim of quantifying the dual chain scission/crosslinking process in polyamides.
- Attention is also paid to physical properties, especially optical (yellowing), suggesting correlation between their changes and oxidation induced structural changes.

2. Experimental

2.1. Material

Unstabilized 70 μm thick PA11 film was prepared at 240 °C from PA11 pellets provided by ARKEMA in a single screw extruder RCP-0750 (Randcastle). This thickness value was chosen to avoid diffusion limited oxidation.

2.2. Accelerated ageings

PA11 films were placed in an air ventilated ovens XUO 32 (France Etuves) at temperature range between 90 and 165 °C. Samples were also aged in autoclaves at 110 °C under oxygen pressure (between 0.3 and 1.6 MPa). The samples were dried overnight under vacuum at 50 °C before aging.

2.3. FTIR spectroscopy

Infrared spectra were collected in transmission mode using a Perkin Elmer Frontier spectrophotometer in the range 4000–400 cm^{-1} at 4 cm^{-1} optical resolution and 32 scan repetitions.

The determination of the imide absorption band in the carbonyl area is carried out by the investigation of diacetamide (D5950 Aldrich), assumed to be a pertinent model compound. Different concentrations of diacetamide are prepared in $CHCl_3$ in order to determine the imide molar extinction coefficient. The solutions were placed in a KBr sealed cell of 100 μm optical path (GS0131 Specac) to perform the IR spectra.

2.4. UV–Visible spectrophotometry

Transmission UV–Visible spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis spectrophotometer between 200 and 800 nm.

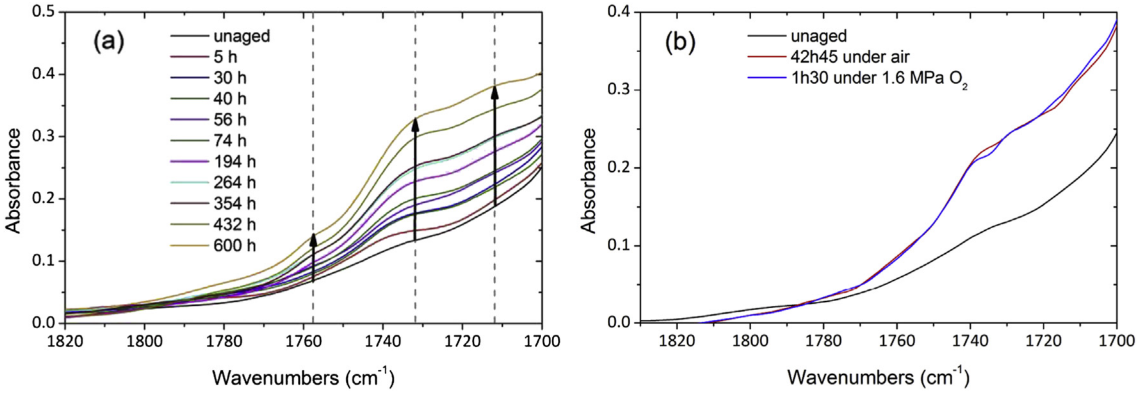

Fig. 2. Carbonyl absorption area during thermal aging of PA11 films under air at 110 °C (a) and comparison of IR spectra during air aging and under oxygen pressure at 110 °C (b).