Polymer Degradation and Stability 98 (2013) 22-36

Contents lists available at SciVerse ScienceDirect



Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Thermal oxidation kinetics of additive free polyamide 6-6

C. El-Mazry^{a,b}, M. Ben Hassine^b, O. Correc^a, X. Colin^{b,*}

^a CSTB, Aquasim, 11 rue Henri Picherit, 44300 Nantes Cedex, France ^b Arts et Metiers ParisTech, Laboratoire PIMM, 151 boulevard de l'Hôpital, 75013 Paris, France

ARTICLE INFO

Article history: Received 3 July 2012 Received in revised form 22 October 2012 Accepted 8 November 2012 Available online 19 November 2012

Keywords: Aliphatic polyamides Thermal oxidation Chain scission Embrittlement Kinetic modeling

ABSTRACT

Thermal aging of an additive free PA 6-6 has been elucidated at 90, 100, 120, 140, 150 and 160 °C in airventiled ovens by Fourier transform infrared spectrophotometry, viscosimetry in molten state and uniaxial tensile testing. Oxidation of methylene groups starts after a considerably shorter induction period but reaches a lower maximal rate than in additive free PE. Cleavage of C–N bonds constitutes the main source of chain scissions. It leads to the formation of aldehyde chain-ends and a catastrophic decrease in molar mass. Embrittlement occurs at a very low conversion ratio of the oxidation process, in particular when the concentration of aldehyde chain-ends reaches a critical value of $[PH=0]_F \approx 5.6 \ 10^{-3} \ mol \ 1^{-1}$, corresponding to a critical value of the number average molar mass of $M_{nF} \approx 17 \ \text{kg} \ \text{mol}^{-1}$. At this stage, the entanglement network in the amorphous phase is deeply damaged.

A non-empirical kinetic model has been derived from the oxidation mechanistic scheme previously established for PE, but improved by adding elementary reactions specific to polyamides such as the rapid decomposition of unstable hydroxylated amide groups. This model describes satisfyingly the main features of the thermal oxidation kinetics of PA 6-6, but also of other types of aliphatic polyamides studied previously in the literature such as: PA 6, PA 12 and PA 4-6, as long as it is not controlled by oxygen diffusion. At the same time, it confirms the existence of an universal character for the thermal oxidation kinetics of aliphatic polyamides whatever their origin, i.e. their initial molar mass, crystallinity ratio, concentration of impurities, structural irregularities, etc.

© 2012 Elsevier Ltd. All rights reserved.

Polymer Degradation and

Stability

1. Introduction

Polyamides (PAs) are increasingly considered for technical applications because of their excellent resistance to mechanical fatigue, friction and many chemical substances (e.g. oils, greases and hydrocarbons), but also their high barrier properties to liquids and gases. They have already found many applications in various industrial sectors such as offshore (e.g. pipes for the transport of oil and natural gas), automotive (e.g. radiators for the cooling of motors) or drinking water distribution (e.g. safety parts in domestic networks). In most cases, PA pieces are exposed in aggressive environments, where they are in contact with chemical reagents such as water, oxygen, chlorine disinfectants, etc., which poses the problem of their long term durability.

Since the late 1950s, many research works have been devoted to hydrolytic aging of PAs e.g. [1-9]. This type of chemical aging is now fairly well understood [10]. Recently, a heuristic kinetic model has been derived from the classical mechanistic scheme for

reversible hydrolysis in order to access to the molecular and macromolecular changes (against time of exposure), but also to the consequences of these changes on morphology and fracture properties [10]. Now, a new challenge is to determine and elucidate the relationships between PAs structure and rate constants of hydrolysis and condensation reactions by using the kinetic model as an inverse method.

On the contrary, too few research works have been devoted to the thermal aging of additive free PAs [8–29] and their model compounds [14,16,20,21,29,30] to be able to define, at the present time, a general approach for lifetime prediction. Moreover, these studies have focused only on certain aliphatic PAs: essentially PA 6 [11–25] and PA 6-6 [8,9,11,12,26–29], but rarely PA 12 [13,15,16] and PA 4-6 [15,28]. Finally, their thermal oxidation mechanisms and kinetics have been investigated by a small number of analytical techniques, in particular: oxygen absorption [8,14–17,20,21,25,28,30], Fourier transform infra-red (FTIR) [17,22,25] and visible/ultra-violet spectrophotometries (Vis–UV) [11,12,16,25,27], nuclear magnetic resonance spectroscopy (NMR) [16], chemical titration [14–17,23,25,27,30], chemiluminescence (CL) [13,15–18,20–22,25,26,29,30] and differential calorimetry under pure oxygen (TIO) [17,19,22].

^{*} Corresponding author. Tel.: +33 1 44 24 61 47; fax: +33 1 44 24 63 82. *E-mail address:* xavier.colin@ensam.eu (X. Colin).

^{0141-3910/\$ –} see front matter \circledcirc 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymdegradstab.2012.11.002

Nevertheless, from the oxidation kinetic curves obtained by plotting the chemical property under consideration versus time of exposure, two important kinetic quantities can be determined graphically (Fig. 1):

- Induction time (*t_i*) would correspond to the period of time during which the effects of oxidation are too small to be detected by common laboratory analytical techniques.
- Maximal oxidation rate (r_S) would correspond to the steadystate oxidation rate if the substrate concentration has not been excessively reduced by the rapid auto-acceleration of oxidation at the end of the induction period [31].

Values of t_i and r_s of additive free PAs have been tentatively compiled between 100 and 200 °C from the literature of the past half century [11,13–23,25–30]. Unfortunately, t_i was too short to be correctly estimated, even from real-time analysis techniques such as oxygen absorption, differential calorimetry (TIO) or chemiluminescence (CL). As a result, only values of r_s deserved to be exploited. As an example, values of r_s determined in air or pure oxygen (under atmospheric pressure) are reported in the Arrhenius diagram of Fig. 2. These values are compared to those determined for another important type of polymethylenic substrate extensively studied in the literature and thus, selected as a reference material in this study: additive free polyethylene (PE) [32,33].

From a kinetic analysis of these experimental data, it is possible to get an idea of the resistance to thermal oxidation of aliphatic PAs compared to PE, but also to highlight the main peculiarities of their oxidation kinetics. In the temperature range under study, one can see that:

 The oxidation kinetics of both types of polymethylenic substrates exhibits an universal character whatever their origin, i.e. their initial molar mass, crystallinity ratio, degree of



Fig. 1. General shape of oxidation kinetic curves. Y designates a chemical quantity changing during thermal aging of hydrocarbon polymers. Graphical determination of induction time (t_i) and maximal oxidation rate (r_s) .



Fig. 2. Arrhenius plot of the maximal oxidation rate (r_s) of additive free aliphatic PAs and PE in air or pure oxygen (under atmospheric pressure) between 90 and 200 °C.

branching, concentration of impurities, structural irregularities, etc.

- r_S obeys an Arrhenius law with a different pre-exponential factor, but almost the same activation energy for both types of polymethylenic substrates (Table 1), which would suggest that there are similarities between their thermal oxidation mechanisms and kinetics.
- Oxidation of methylene groups starts from the early periods of exposure in aliphatic PAs, whereas it starts after a well-marked induction period in PE. In contrast, the maximal oxidation rate is significantly lower (about 20–100 times lower) in aliphatic PAs than in PE.

Such differences can be tentatively explained by using, in a first approach, relatively simple kinetic equations derived from the classical version of the standard oxidation scheme at low to moderate temperatures (typically for T < 200 °C) in oxygen excess [34]. In such thermal aging conditions, oxidation is essentially initiated by the bimolecular decomposition of hydroperoxide groups (POOH) [35]. Then, t_i and r_s can be expressed by [35]:

$$t_i = \frac{1 - \ln Y_0}{\sqrt{2r_S k_{1b}}} \quad \text{with } Y_0 = \frac{[\text{POOH}]_0}{[\text{POOH}]_S}$$
(1)

$$r_{\rm S} = \frac{k_3^2 [PH]^2}{2k_{\rm 6 app}} \tag{2}$$

where k_{1b} , k_3 and k_6 app are initiation, propagation and apparent termination rate constants respectively. [POOH]₀ and [POOH]_S are initial and steady-state concentrations of POOH respectively. [PH] is the concentration of oxidizable CH groups in the amorphous phase. Examples of [PH] values for aliphatic PAs and PE have been reported in Table 2.

According to these equations, only a combination of high values of k_{1b} and $k_{6 app}$ would allow to obtain simultaneously low values of t_i and r_s . This important result can be interpreted as follows: Hydroperoxide groups (POOH) would be more unstable and

Table 1

Arrhenius parameters: pre-exponential factor (r_{S0}) and activation energy (E_S), for maximal oxidation rate (r_S) of additive free aliphatic PAs and PE in oxygen excess between 90 and 200 °C.

Polymers	$r_{\rm S0} ({\rm l}\;{\rm mol}^{-1}\;{\rm s}^{-1})$	E_S (kJ mol ⁻¹)
PE	$5.5 imes 10^{13}$	138
PAs	$1.4 imes10^9$	115

Download English Version:

https://daneshyari.com/en/article/5202428

Download Persian Version:

https://daneshyari.com/article/5202428

Daneshyari.com