



Kinetic analysis of polydicyclopentadiene oxidation



Virginie Defauchy^a, Pierre Yves Le Gac^b, Alain Guinault^a, Jacques Verdu^a, Gilles Recher^c, Renata Drozdak^c, Emmanuel Richaud^{a,*}

^a Laboratoire PIMM, Ensam, CNRS, Cnam, 151 boulevard de l'Hôpital, 75013 Paris, France

^b IFREMER Centre de Bretagne, Marine Structures Laboratory, BP70, 29280 Plouzane, France

^c TELENE SAS, 2 rue Marie Curie, 59910 Bondues, France

ARTICLE INFO

Article history:

Received 21 April 2017

Received in revised form

30 May 2017

Accepted 7 June 2017

Available online 10 June 2017

Keywords:

Polydicyclopentadiene

Thermal oxidation

Segmental mobility

Catalysis

Diffusion limited oxidation

ABSTRACT

The *in situ* thermal oxidation of thin unstabilized polydicyclopentadiene was studied by TGA to monitor mass gain, and DSC to characterize hydroperoxides concentration. Results were discussed using kinetic analysis, which allowed the estimation of activation energies for key reactions of the oxidation process. Activation energy for termination was shown to be higher than in hydrocarbon liquids, which was discussed from the theory of diffusion controlled reactions, and a possible link with local motions associated with sub-glassy transition. Activation energy of thermal decomposition of hydroperoxides was found lower than for model hydroperoxides, suggesting an accelerating effect of organometallic catalysts. Despite those two results that indicate a poor thermal stability of thin pDCPD films, measurements of oxygen diffusivity at several temperatures show that oxidation remains confined in a relatively thin surface layer which would allow the pDCPD properties to be preserved.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

In the case of a single bimolecular radical reaction: $A^\circ + B^\circ \rightarrow$ inactive species, the rate of radical depletion depends on: ① their initial concentration, i.e. the average distance between the closest reactant molecules; ② the rate at which they move into the reactive medium (expressed in terms of diffusion coefficient); ③ geometric and thermochemical factors determining the probability to react. These later can be expressed for instance as the capture radius in the Waite's theory [1,2].

The domain of high reactant concentrations and high reactant mobility corresponds to the domain of classical chemical kinetics. Bimolecular rate constants only depend on geometric and thermochemical factors but are independent of time and reactant concentrations. When the concentration or the mobility of reactants decreases, the system reaches a limit beyond which the rate constant begins to fall because the time between encounters becomes a non-negligible fraction of the whole reaction time. Here, it is better to consider that the reactivity is ruled by an apparent rate constant depending in part on the diffusivity of macroradicals.

Polydicyclopentadiene (pDCPD) is from this point of view quite attracting. It is obtained by metathesis of dicyclopentadiene. This polymerization mechanism (awarded by Nobel Prize in 2005 [3,4]) allows the production of a bulky material from a low viscosity reactive mixture in a short processing time (ca 1 min) without external heating. Beside those practical advantages for designing thermosets, pDCPD is interesting from the “degradation” point of view because of its high level of double bonds together with a glassy behavior (its T_g is close to 160 °C). In other words, it offers the double interest:

- to investigate the possible “tradeoff” between its easy polymerization and its oxidative stability.
- to study theories on diffusion controlled reactions.

In a recent paper [5], the rate constants of pDCPD oxidation reactions were estimated from the simulation of carbonyls and hydroperoxides curves and linked with the possible origins of pDCPD oxidizability. It was shown that both high initiation rate constants and low termination rate constants were needed to simulate the kinetic curves for carbonyls and hydroperoxides under air. Our paper left several questions which still are unanswered among which:

* Corresponding author.

E-mail address: emmanuel.richaud@ensam.eu (E. Richaud).

- how can we determine the kinetic parameters using a different approach than their adjustment from experimental curves performed in Ref. [5] in order to confirm the previous findings?
- what happens in the case of thick samples?
- what are the consequences of oxidizing at glassy state on termination reactions, i.e. which reactions ($P^\bullet + P^\bullet \rightarrow \dots$, $POO^\bullet + P^\bullet \rightarrow \dots$, $POO^\bullet + POO^\bullet \rightarrow \dots$) are impacted? Which mechanisms rule the macromolecular mobility, and what is the role of this later in degradation mechanisms and kinetics? This last question was scarcely addressed in existing papers (see for example [6,7]) and remains for us open in the field of polymer degradation.

We try here to answer those questions by investigating the pDCPD degradation kinetics in the temperature range [$T_g - 100$ °C; T_g]. Given the relative fastness of degradation, we have chosen to monitor ageing only by *in situ* techniques: mass uptake by TGA, and quantification of peroxides using DSC (with direct oxidation of the polymer in DSC cell). Those analyses will be completed with oxygen permeability measurements to understand the control of oxidation by oxygen diffusion. Comparisons will often be done with polybutadiene which has a comparable double bonds concentration but being aged and used in its rubbery state. Last, particular attention will be addressed to the existence of Diffusion Limited Oxidation (DLO) [8] so as to extract reliable kinetic parameters (i.e. only when samples are not subjected to DLO effects).

2. Experimental

2.1. Material

Material from 5 cm stabilized pDCPD plate was cut in 5–100 μm thin films using a Reichert-Jung microtome. The films were purified by refluxing in CH_2Cl_2 overnight and then stored in fridge prior to exposure. As received 175 μm stabilized films provided by the supplier were used for permeability measurements.

2.2. Ageing and characterization

2.2.1. Thermogravimetric analysis (TGA)

Isothermal gravimetric measurements were monitored using a TGA Q50 (TA Instruments) driven by Q Series Explorer. About 0.1 mg samples were placed in a Platinum pan which was heated under nitrogen till to the measurement temperature (from 105 °C to 150 °C) at which cell atmosphere was switched to nitrogen-oxygen mixtures with oxygen ratio from 0% to 100% (using a Gas-Mix device). Results were analyzed using TA Analysis software.

2.2.2. *In situ* hydroperoxides titration by differential scanning calorimetry (DSC)

Samples were directly oxidized in DSC cell so as to quantify peroxides using the following procedure:

- heating to the ageing temperature under nitrogen (10 °C min^{-1}).
- isothermal ageing under 1 bar of oxygen at temperatures ranging from 50 to 120 °C.
- cooling down to room temperature under nitrogen (10 °C min^{-1}).
- heating to 280 °C under nitrogen (10 °C min^{-1}).

Analyses were done using a DSC Q10 apparatus (TA Instruments) with Aluminum pans (the lid was manually drilled to ensure the access of oxygen) under 50 ml min^{-1} flow of oxygen or nitrogen. Only one single pDCPD foil (about 0.2 mg) was used to avoid complications due to Diffusion Limited Oxidation. Results

were analyzed using TA Analysis software.

2.2.3. Permeability

As received 175 μm thin pDCPD films maintained in a mask (with an accessible surface ca 5 cm^2) were placed between the two compartments of a Systech 8001 permeameter. The cell and the sample were completely purged during one week in order to avoid oxygen diffusivity underestimation due to residual oxygen present in the polymer bulk. Purge was performed at room temperature to avoid *in situ* oxidation. Pure oxygen (99.9%) was then introduced into the upper half of the chamber while an oxygen-free carrier gas flowed through the lower half. A coulometric sensor monitored the oxygen flow through the sample induced by oxygen pressure difference.

The onset time (or time lag) τ expresses the time which is necessary for oxygen to go across the sample. The analytical solution of Fick's law in a case of an infinite plate of thickness L with penetrant at a C_s concentration on one edge and 0 at the other allows to determine the diffusion coefficient of oxygen by the equation [9,10]:

$$\tau = L^2 / 6D_{O_2} \quad (1)$$

Measurements were performed at 23, 35, 40 and 50 °C.

3. Results

3.1. Thermogravimetric results

Gravimetry is a simple technique for characterizing polymer oxidation [11–14] and measure the increase in mass induced by the grafting of oxygen on the polymer skeleton. This sensitive and *in situ* technique thus allows following a simple and reliable manner the oxidation kinetics.

3.1.1. Effect of sample thickness

Samples with thicknesses ranging from 5 to 150 μm were aged at 120 and 150 °C under 1 bar O_2 so as to determine the maximal thickness below which oxidation is not controlled by oxygen diffusion. TGA curves are presented in Fig. 1a. At 150 °C, the induction period duration is negligible (less than 5 min) and the rate of mass uptake (linked to the oxidation rate r_{OX} as shown in "APPENDIX") reaches rapidly its maximal value (r_m). The maximal rate seems almost constant for samples having a thickness lower than ca 20 μm (Fig. 1b) which corresponds here to twice the Thickness of Oxidized Layer (TOL) [11–13]. In the following, TOL will hence be assumed higher than 10 μm for temperatures lower than 150 °C, since the temperature dependence for oxidation rate is higher than for oxygen diffusion (as discussed later). This is consistent with the value ca 15 μm observed at 120 °C (Fig. 1b).

3.1.2. Effect of temperature

In order to consider the temperature effect on oxidation rate of pDCPD, mass uptake for 20 μm thin samples were recorded at several temperatures ranging from 105 to 150 °C under 1 bar of O_2 . TGA curves (Fig. 2) are characterized by:

- an induction period, the duration of which decreases when increasing temperature.
- an auto-acceleration till to a maximal oxidation rate value which increases with temperature.
- a plateau ca 25% which is in a first approach independent of the ageing temperature.
- a small mass loss can be observed. It seems to be masked by the oxidation induced weight increase at 150 °C. In the absence of

Download English Version:

<https://daneshyari.com/en/article/5200662>

Download Persian Version:

<https://daneshyari.com/article/5200662>

[Daneshyari.com](https://daneshyari.com)