



## Thermooxidative aging of polydicyclopentadiene in glassy state



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### ARTICLE INFO

#### Article history:

Received 10 December 2013

Received in revised form

8 January 2014

Accepted 26 January 2014

Available online 11 February 2014

#### Keywords:

Polydicyclopentadiene

Thermal oxidation

Kinetics

Molecular mobility

### ABSTRACT

Thermal aging of thin films of unstabilized polydicyclopentadiene (pDCPD) at several temperatures ranging from 120 to 30 °C was investigated by means of carbonyl build up by FTIR with ammonia derivatization, double bond titration, mass uptake measurement, hydroperoxides titration by iodometry and DSC coupled with sulfur dioxide treatment. In the temperature range under investigation, pDCPD is in glassy state and it oxidizes faster than common polymers oxidized at rubbery state (e.g. polydienic elastomers). Using the kinetic analysis, these results were ascribed to increased initiation rate due to catalyst residues, some possible intramolecular processes favoring propagation, or a very low termination rate of oxidation radical chains because of the control of termination reactions by macroradical diffusion.

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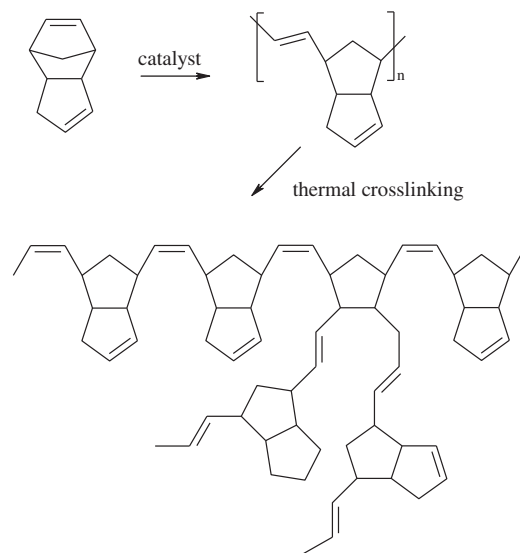
### 1. Introduction

Most of the knowledge on polymer oxidation mechanisms and kinetics was obtained from experimental studies on elastomers [1,2] or semi-crystalline polyolefins [3,4]. The oxidation of all these materials occurs in a rubbery/liquid phase characterized by relatively fast cooperative segmental motions. However, some authors [5,6] have assumed that bimolecular processes between macromolecular reactive species may be disadvantaged because of low diffusivity of these species in such highly viscous matrices. In other words, radical propagation of the oxidation process would not be limited by bimolecular termination processes. It was actually observed that the ratio  $k_p^2/k_t$  expressing oxidizability was higher for PP than for its model compounds [7]. A possible explanation is that rate constant propagation  $k_p$  has same value in polypropylene (PP) and its liquid model compounds whereas termination constant  $k_t$  is higher in liquids than in PP amorphous phase. Propagation actually involves a reaction between a peroxy radical and a close monomer unit and so should not be controlled by diffusion whereas termination involves a reaction between two species (peroxy radicals) at low concentration and may be controlled by diffusion so that its rate depends sharply of the medium viscosity.

In the case of polymers in glassy state, extremely low termination rates and then extremely high oxidation rates are thus expected. Unfortunately, kinetic studies of the oxidation of glassy polymers are scarce. In the case of aromatic polymers [8], significant oxidized layer (100 μm) were observed despite a slow

propagation (linked to strong C–H bonds), which militates in favor of termination control by diffusion. A comparison of hydrocarbon elastomers oxidation in rubbery state with oxidation of hydrocarbon glassy polymers at the same temperature would bring another evidence of the molecular mobility effect on oxidizability. This is the reason why pDCPD has been chosen here.

pDCPD is synthesized from Ring Opening Metathesis Polymerization of dicyclopentadiene:



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After thermal crosslinking [9–11], it gives a network with a glass transition temperature of ca 160 °C used for instance in off-shore applications [12]. Apart some irregularities [9–11], its structure displays highly reactive groups: double bonds able to react by addition reactions and easily abstractable allylic hydrogens.

The present study is limited to unstabilized pDCPD thin films (not submitted to Diffusion Limited Oxidation), i.e. materials not aimed at any industrial purpose, exposed to temperatures ranging from 30 to 120 °C to illustrate the specificity of oxidation in glassy state.

## 2. Experimental

### 2.1. Material

Samples were supplied as stabilized bulk material prepared by casting dicyclopentadiene into an aluminum mould preheated at 40 °C. The catalyst of the metathesis polymerization is a ruthenium salicylaldehyde phenylindenyliene complex. Material was cut in 20–30 µm slices using a Reichert-Jung microtome. These ones were purified by refluxing in CH<sub>2</sub>Cl<sub>2</sub> overnight. Unstabilized samples were stored in fridge prior to exposure.

### 2.2. Exposure conditions

Samples were exposed in ventilated ovens at various temperatures ranging from 120 to 30 °C.

### 2.3. Characterization

#### 2.3.1. Fourier Transform InfraRed spectroscopy

FTIR spectra in transmission mode were obtained on free standing films in transmission mode by averaging 4 scans at a 2 cm<sup>-1</sup> resolution using a Frontier apparatus (Perkin Elmer) driven by Spectrum software.

#### 2.3.2. SO<sub>2</sub> treatment

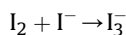
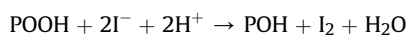
Sulfur dioxide treatments were performed by putting samples during 24 h in closed vessels in which SO<sub>2</sub> was in situ generated from solutions of 40 mg of Na<sub>2</sub>SO<sub>3</sub> (S0505 grade – Sigma Aldrich) in HCl (analysis grade 37% – Carlo Erba) [13].

#### 2.3.3. NH<sub>3</sub> treatment

NH<sub>3</sub> treatments were performed by putting samples during 24 h in closed vessels in which NH<sub>3</sub> was in situ generated by combining equimolar solutions of NH<sub>4</sub>Cl and NaOH [8].

#### 2.3.4. Iodometry

Hydroperoxides react with iodine anions in isopropanol using acetic acid for acidizing the media by the following reaction [14–16]:



A mass  $m$  (about 1 mg) of oxidized pDCPD was placed in 7 ml 10:1 isopropanol:acetic acid mixture in a bicol flask (isopropanol: ref 34959 HPLC grade purity 99.9% – Sigma Aldrich, acetic acid: ref A6283 purity > 99% – Sigma Aldrich). When the mixture reached refluxing temperature, I<sup>-</sup> was brought by adding 3 ml of a saturated solution of NaI (ref 409286 – Sigma Aldrich) saturated solution in isopropanol. After a 10 min reaction time, solution was analyzed by UV spectroscopy (Perkin Elmer Lambda 35) in 1 cm UV cell. Hydroperoxides concentration was thus calculated from the I<sub>3</sub><sup>-</sup>

absorbance at 355 nm (DO<sub>355</sub>) using a molar absorptivity  $\epsilon = 25,000 \text{ l mol}^{-1} \text{ cm}^{-1}$  by the formula:

$$[\text{POOH}] = 0.4 \times \frac{\text{DO}_{355}}{m}$$

[POOH] being here expressed in mol kg<sup>-1</sup> and  $m$  in mg.

### 2.3.5. DSC

Thermal analysis was performed using a Q10 DSC apparatus (TA Instrument) driven by Q Series Explorer software. DSC was first calibrated with an indium standard. Approximately 1 mg of virgin or oxidized sample was heated from 25 to 300 °C in sealed aluminum pans, at a heating rate of 10 °C min<sup>-1</sup> under an inert atmosphere obtained by purging cell with a 50 ml min<sup>-1</sup> nitrogen flow. Results were processed using the TA Analysis software.

### 2.3.6. Thermogravimetric analysis

Gravimetric measurements were monitored using a TGA Q50 (TA Instrument) driven by Q Series Explorer. About 10 mg samples were placed in a Platinum pan which first heated under nitrogen till to the measurement temperature at which cell atmosphere was switched to oxygen or nitrogen-oxygen mixtures (GasMix). Results were processed using TA Analysis software.

## 3. Results

### 3.1. Gravimetric study

Mass variation has been monitored for samples exposed at 120 °C under 21, 50, 75 and 100% of the atmospheric pressure (Fig. 1).

The mass increases continuously which is a characteristic of unsaturated polymers [1,2,17]. The rate of mass gain is maximal shortly (1–2 min) after the beginning of exposure, and then decreases continuously.

It is possible to distinguish two periods corresponding to distinct phases of the oxidation process:

- An “initial” period, with a characteristic time of the order of 10–20 min decreasing with oxygen pressure.
- A “final” period with a characteristic time at least 10 times higher than “initial” one.

The mass gain reaches about 10–15% at the end of the first period that corresponds to  $1 \pm 0.2$  oxygen atoms per initial monomer unit.

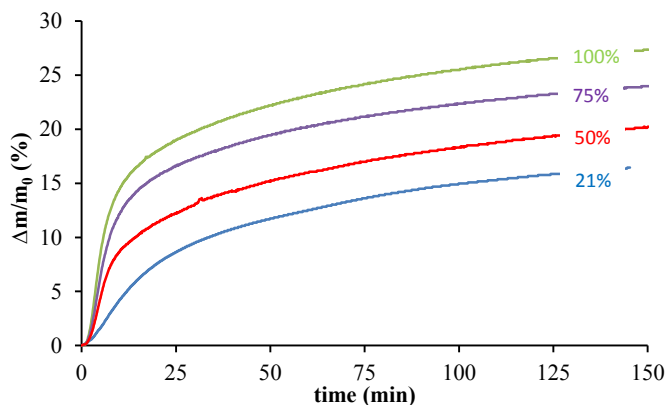


Fig. 1. Kinetics of mass uptake at 120 °C for pDCPD under several oxygen concentrations.

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