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## Thermo-oxidative stability of electron beam irradiated ethylene norbornene copolymer

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### HIGHLIGHTS

- ENC is a brand new polymer with good chemical and radiation resistance.
- Thermo-oxidation of ENC is evaluated by DSC and TGA after electron beam irradiation.
- OIT measurements are correlated to antioxidant concentration.
- Effect of radiation dose on thermo-oxidation is highlighted.
- Activation energies of oxidation are calculated.

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### ABSTRACT

The effect of ionizing radiation on the thermal stability of ethylene norbornene copolymer (ENC) to which a phenolic antioxidant (AO), Irganox 1010<sup>®</sup>, had been added, was investigated. To this end, a series of appropriate thermal analyzes methods (TGA, DSC, OIT measurements), were used for testing the polymer matrix oxidation level. We were able to correlate the diminution of AO concentration with the oxidation induction time and calculate the activation energy, thereby demonstrating the efficiency of the AO and the effect of radiation.

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## 1. Introduction

The oxidative stability of organic materials containing antioxidants can be directly assessed using thermal analysis. Thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) evaluate the thermal stability of polymers and are referred as quality control techniques described in ISO standards (AFNOR-NF-EN-ISO-11357-6, 2013). OIT measurements are simple and commonly used methods that give information on polymer stability, antioxidant protection and degradation level. In this study a hindered phenolic antioxidant (Irganox 1010<sup>®</sup>), known to be widely used in polyolefins for resistance towards oxidation, is added to ENC. ENC, which is a quite new polymer, possesses good chemical resistance and biocompatible properties (Petryl et al., 2010; Polanska et al., 2010). This makes it well suited for medical

and pharmaceutical applications (blister packs, pre-filled syringes, etc.). As far as we are aware, few studies have reported on the consequences of ionizing radiation on ENC and especially no study deals with the thermo-oxidative stability of ENC.

## 2. Experimental

ENC was supplied by Ticona under the trade name TOPAS<sup>®</sup> 8007/S-41 as films, 200 μm thick. This ENC grade is totally amorphous and has a norbornene molar percentage of 35%. Two batches of ENC were used in this study: one containing Irganox 1010<sup>®</sup> as antioxidant (called "Add") at a concentration of 1180 ppm, and one without any additive (called "Add-free"). Chemical structures of ENC and Irganox 1010<sup>®</sup> are given in Figs. 3 and 4 respectively.

Irradiations were performed using an electron beam produced by a high power generator (10 MeV) from a 10 kW power accelerator (Ionisos, France). The dose range was from 25 to 150 kGy

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and irradiation was performed on samples packed in paper bags at ambient conditions. The dose of 25 kGy was obtained after one passing under the electron beam on a tray having a speed of 0.9 m/min. Dosimetry was checked following the corresponding guideline (AFNOR-NF-EN-552, 1994).

Thermal properties of the samples were studied by using a temperature- and energy-calibrated TA Instruments Q1000 differential scanning calorimeter (DSC) as well as a TA instruments Q500 thermogravimetric analyzer (TGA). The standard deviations in the different measurements were estimated by analyzing between three and five different samples.

For DSC measurements, each sample (mass between 8 and 10 mg) was enclosed in a 50 mL standard aluminum crucible with three holes in the cover. Whatever the gas used for the experiments, the gas flow rate was of 50 mL min<sup>-1</sup>.

For the determination of the glass transition temperature ( $T_g$ ), the experiments were assessed by recording the calorific capacity variation under nitrogen atmosphere at a rate of 20 °C min<sup>-1</sup> after a heat/cool/heat cycle. For the OIT measurements, each sample was firstly treated in a dynamic way that means it was heated from 30 °C to 120 °C at a rate of 20 °C min<sup>-1</sup> under nitrogen atmosphere, allowed to rest for 5 min before the atmosphere was switched to pure oxygen and then heated again with the same flow rate. The temperature was then elevated up to 300 °C in order to evaluate the most suitable oxidation temperature, also called OIT<sub>temp</sub> (Schmid et al., 2006), that will be used for the further OIT determination. A common OIT<sub>temp</sub> was chosen for fitting all ENC samples that was of 215 °C. In a second step, OIT measurements were performed at the given temperature (OIT<sub>temp</sub>) and the exothermal oxidation was then recorded. The oxidation induction time (OIT) was determined as the time to the intersection between the isothermal baseline and the tangent from the maximum derivative after oxidation has started (see Fig. 3) (AFNOR-NF-EN-ISO-11357-6, 2013; Focke and van der Westhuizen, 2010; Grenet and Legendre, 2010; Schmid et al., 2006).

For TGA measurements, each sample (mass between 5 and 10 mg) was heated from ambient temperature up to 600 °C under nitrogen atmosphere at a rate of 10 °C min<sup>-1</sup>. In the case of the experiment done under oxygen atmosphere, samples were enclosed in DSC 50 mL standard aluminum crucible with holes enlarged by scissors in the cover in order to allow gas transport to the sample without measuring the temperature variation due to sample oxy-combustion (Haykiri-Acma et al., 2010). Whatever the gas used for the experiments, the gas flow rate was of 50 mL min<sup>-1</sup>.

**Additives extraction:** To identify and quantify the additives in the polymer, we used a dissolution/precipitation process. 3 g of ENC granules were dissolved at reflux in toluene under stirring and after complete dissolution, the polymer was precipitated by slowly adding methanol under stirring as described earlier (Barakat et al., 2013; Saunier et al., 2008). Solutions containing additives, oligomers and degradation products were then evaporated and the extraction solution was afterwards analyzed by HPLC. The quantification of the phenolic antioxidant (Irganox 1010<sup>®</sup>) found in the polymer was validated by establishing a calibration curve. Irganox 1010<sup>®</sup> concentrations are given in Table 1.

### 3. Results and discussion

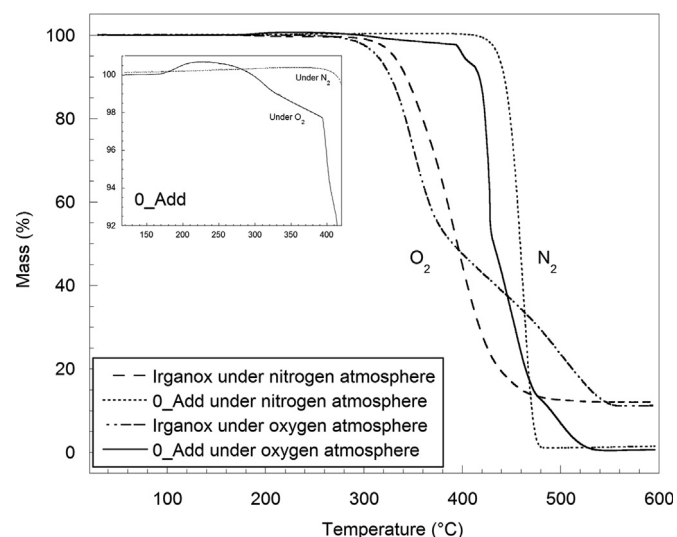
#### 3.1. Measurements under N<sub>2</sub>

DSC measurements evidenced a glass transition temperature ( $T_g$ ) at around 82 °C for additive-free samples and at around 80 °C for other samples. Considering the standard variation, the dose did not seem to have any effect on the  $T_g$  value (see Table 1).

**Table 1**

Thermal experiments performed under nitrogen atmosphere. Irganox 1010<sup>®</sup> concentrations, glass transition ( $T_g$ ), maximum temperature of degradation ( $T_{max}$ ) and mass loss at 600 °C are given as a function of the absorbed dose.

ENC reference	Dose (kGy)	[Irganox 1010] (ppm)	$T_g$ (°C) (n=3)	$T_{max}$ (°C) (n=3)	Mass loss@600 °C (%)
0_Add free	0	0	82.3 ± 0.1	462.0 ± 0.3	99.3 ± 0.3
0_Add	0	1180	80.6 ± 0.2	461.0 ± 0.2	99.5 ± 0.3
25_Add	25	290	80.4 ± 0.6	461.0 ± 0.3	99.2 ± 0.3
75_Add	75	50	79.9 ± 0.6	461.1 ± 0.4	99.0 ± 0.3
150_Add	150	< 0.2	79.9 ± 0.2	461.1 ± 0.1	99.6 ± 0.1
Irganox 1010	0	-	-	355/393	22/65



**Fig. 1.** Comparison of TGA curves under nitrogen and oxygen of a non-irradiated sample (0\_Add) and of Irganox 1010<sup>®</sup>. The zoom shows the TGA curves between 120 and 420 °C and evidences the mass increase of ENC under oxygen atmosphere.

TGA measurements showed one main reaction stage from 400 to 480 °C. The degradation temperature ( $T_{max}$ ) was measured at about 461 °C and was obtained by the maximum temperature of the first derivative signal (see Table 1 and Fig. 1).  $T_{max}$  did not evolve with the dose and a total mass loss at 600 °C was observed whatever the sample. In the same experimental conditions, Irganox 1010<sup>®</sup> was degraded at a much lower temperature ( $T_{max}$ =393 °C with a shoulder at 355 °C).

#### 3.2. Measurements under O<sub>2</sub>

The effect of the experimental atmosphere on TGA curves are depicted in Figs. 1 and 2. Curves obtained under oxygen atmosphere are very different from those obtained under nitrogen: First of all, under oxygen, we observed a small mass increase (less than 1% mass) due to oxygen uptake at about 225 °C, which can be associated, according to (Camacho and Karlsson, 2002; Gal et al., 1983), to the formation of hydroperoxides and peroxy radicals. As temperature increased, they were converted into labile products and disappeared for higher temperatures. Then, a slow mass decrease was observed between 300 and 400 °C, followed by 4 steps, the first and last ones being the smallest (see Table 2 and Fig. 2).  $T_{max}$  are about 390, 420, 450 and 500 °C. In the same experimental conditions, Irganox 1010<sup>®</sup> was degraded in two steps with  $T_{max}$  of 345 °C and 502 °C.

Under oxygen atmosphere, both the degradation of ENC and Irganox 1010<sup>®</sup> started for lower temperatures than under nitrogen

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