



Material Characterisation

Quantification of hindered phenols in polyamide 11 during thermal aging



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ABSTRACT

Polyamide 11 films stabilized by Irganox[®] 1098, Irganox[®] 1010 or Irganox[®] 245 were subjected to thermal oxidation at 110 °C. The residual phenol content was assessed by comparing three analytical methods: high performance liquid chromatography (HPLC), determination of the Oxidation Induction Time (OIT) and Onset Oxidation Temperature (OOT) by thermal analyses. Both OIT and OOT are reliable for virgin PA11 after a relevant calibration by HPLC measurement. In the case of oxidized samples, OOT measurements have the benefits of being more easily interpretable than OIT and less time-consuming than HPLC measurements.

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1. Introduction

Aliphatic polyamides with long alkyl chains such as polyamide 11 (PA11) or polyamide 12 (PA12) offer a sophisticated solution for material design in particular due to their elevated stress at break (>60 MPa) together with their high elongation at break (<300%). The amide group increases cohesive energy but induces a lower thermal stability due to destabilizing effects on the vicinal CH₂ group (also called α -CH₂). Therefore, polyamides cannot be used without stabilizers such as hindered phenols.

The quantification of the concentration of unreacted hindered phenols in polyamides is thus of key importance:

- For quality purpose in order to determine the amount of stabilizers after processing.
- For lifetime assessment: since the depletion of stabilizer concentration results in faster propagation reactions leading to hydroperoxides (being the main source of chain scissions and subsequent embrittlement), it is considered that polyamides can no longer be used once phenols are totally reacted.

Stabilizer detection methods can be divided into three main families:

- Spectroscopic methods such as FTIR and UV. These techniques are based on the monitoring of an absorption band which is specific for the stabilizer, and distinct from polymer matrix absorption bands. FTIR and UV measurements have the great advantage of being performed directly on the solid polymer allowing *in situ* monitoring during aging experiments [1–4].
- Chromatographic method namely (HPLC) that requires a careful sample preparation since stabilizers have to be isolated from the polymeric matrix. The detection modes are generally UV–vis or mass spectroscopy that can be considered as a precise quantitative chemical detection [5–10]. Depending on the detection mode, the degradation products of some stabilizers can also be detected [11].
- Thermal analysis is reported to be particularly simple and very often used to study polyolefin degradation. OIT (Oxidation Induction Time) is usually employed as a routine experiment to characterize the isothermal oxidation [12,13], to determine the efficiency of stabilizers [14,15] and to follow their consumption during oxidation [16–19]. According to Howard [12] and Rosa [20], OIT is very dependent on the experimental conditions (sample size, gas flow, heating rate ...). In order to avoid some

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limitations of this technique especially in the case of polymers having very low OIT such as unstabilized polypropylene, some authors determine the OIT* (Oxidation Induction Temperature) or the OOT (Oxidation Onset Temperature) by performing dynamic thermal analysis in the oxygen or air atmosphere [21–23].

Since this issue was scarcely addressed in the literature for aliphatic polyamides, the aim of this paper is to compare HPLC and thermal analysis to assessing hindered phenol stabilizer concentration in stabilized PA11 films during thermal aging.

2. Experimental

2.1. Materials

Stabilized polyamides were obtained by mixing pure PA11 (BESNO grade presented in Ref. [24]) with three phenol stabilizers differing from the chemical structure and the molecular weight were studied: Irganox[®] 1098, Irganox[®] 1010 and Irganox[®] 245 (Table 1).

In our case, Irganox[®] 1098 was considered as the reference stabilizer because it is commonly used for stabilization of polyamides since the presence of the amide function improves its compatibility with the polymer matrix [25]. Therefore, four materials with various Irganox[®] 1098 concentrations were prepared to investigate on the influence of phenol concentration on oxidation. The composition of the stabilized PA11 film samples is described in Table 2.

The initial concentration of effective stabilizing function (phenol function in our case) is noted [AH] and is given by the following equation [26]:

$$[AH] = \left(\frac{1}{1 - x_C} \right) \cdot \left(f_{AH} \times \frac{\rho_{PA11}}{M_{Stab}} \times x_{Stab} \right) \quad (1)$$

Where x_C is the crystallinity ratio, ρ_{PA11} the density of PA11 in the amorphous phase (1.013 kg L^{-1}), M_{Stab} the stabilizer molar mass, x_{Stab} the global stabilizer weight ratio and f_{AH} the stabilizer functionality (equals to 2 for the Irganox[®]1098 and Irganox[®] 245, and 4 for Irganox[®] 1010). The term $1/(1-x_C)$ expresses the fact that

stabilizer only dissolves into polymer amorphous phase.

Polyamide 11 (BESNO grade) and stabilizers were mixed as a dry blend prepared to follow the composition. The powder blend was processed into pellets by the double screw extruder (HAAKE 2) prior to prepare the film in a single screw extruder at $240 \text{ }^\circ\text{C}$ (Randcastle).

2.2. Characterization

2.2.1. HPLC

The extraction of antioxidant from the polymeric matrix was performed by a dissolution/precipitation method described as follows:

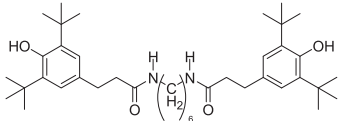
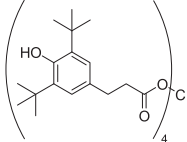
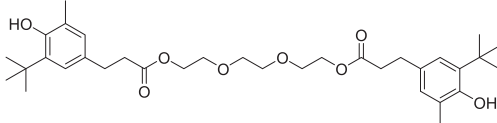
A flask containing the polymer (200–500 mg) with 2 mL of 1,1,1,3,3,3-hexafluoroisopropanol ($\geq 99\%$ purity GC grade, 105228 ALDRICH) was placed in an ultrasonic bath (3–5 h). After the dissolution, the polymeric matrix was precipitated by the addition of 3 mL of dichloromethane ($\geq 99.7\%$ purity HPLC grade stabilized, VWR) and 15 mL of methanol ($\geq 99.8\%$ purity HPLC grade, VWR) with a gentle manual agitation and the flask was allowed to rest for 24 h. The solution was filtered over an Acrodisc CR PTFE $0.2 \mu\text{m}$ (PALL Light Sciences) to perform the chromatographic measurements.

The chromatographic separation was carried out using an Agilent 1100 series HPLC equipped with a UV detector (280 nm). The analytical column was ThermoScientific Hypersil[™] ODS C18 ($125 \text{ mm} \times 4 \text{ mm ID}$) filled with grafted silica, with the particle size being equal to $5 \mu\text{m}$ with 120 \AA pore size. The mobile phase was methanol. Constant flow rate of 1.0 mL min^{-1} was used and the injection volume was $10\text{--}20 \mu\text{L}$. The quantitative identification was calibrated with formerly prepared solutions of the antioxidant under study.

2.2.2. Thermal analysis

In the following, we intend to verify the relevancy of OIT in the case of polyamides and their degradation. PA11 film samples ($\sim 5 \text{ mg}$) were characterized by classical OIT measurements at $190 \text{ }^\circ\text{C}$ by the DSC Q20 apparatus (TA Analysis) driven by Q Series Explorer. The procedure was a ramp temperature of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen ($50\text{--}190 \text{ }^\circ\text{C}$) followed by a 5 min isotherm under

Table 1
Hindered phenol stabilizers used in this study.

Stabilizer ref.		M (g mol^{-1})
Irganox [®] 1098 (CAS Reg N° 23128-74-7)		637
Irganox [®] 1010 (CAS Reg. N° 6683-19-8)		1178
Irganox [®] 245 (CAS Reg. N° 36443-68-2)		586

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