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.

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 CH_2 group (also called α-CH_2). 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

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]:

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

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 °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 (≥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 (≥99.7% purity HPLC grade stabilized, VWR) and 15 mL of methanol (≥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 μm (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 mm × 4 mm ID) filled with grafted silica, with the particle size being equal to 5 μm with 120 Å pore size. The mobile phase was methanol. Constant flow rate of 1.0 mL min^{-1} was used and the injection volume was 10−20 μL. 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 (~5 mg) were characterized by classical OIT measurements at 190 °C by the DSC Q20 apparatus (TA Analysis) driven by Q Series Explorer. The procedure was a ramp temperature of 10 °C min^{-1} under nitrogen (50−190 °C) followed by a 5 min isotherm under

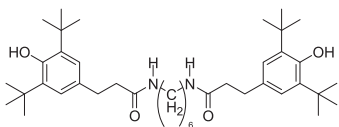**Table 1**
Hindered phenol stabilizers used in this study.

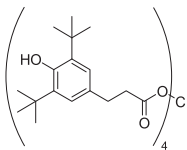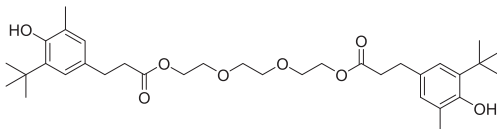| Stabilizer ref.		M (g mol^{-1})
Irganox® 1098 (CAS Reg N° 23128-74-7)		637
Irganox® 1010 (CAS Reg. N° 6683-19-8)		1178
Irganox® 245 (CAS Reg. N° 36443-68-2)		586

Sample	Stabilizer	x_{Stab} (% wt.)	[AH] (mol L^{-1})	M_{n0} (kg mol^{-1})	M_{w0} (kg mol^{-1})	PI
BESNO	−	−	−	19.8	39.7	2.0
BESNO 1	Irganox® 1098	0.02	$8.51 \cdot 10^{-4}$	21.3	43.1	2.0
BESNO 2	Irganox® 1098	0.04	$1.63 \cdot 10^{-3}$	22.7	47.5	2.2
BESNO 3	Irganox® 1098	0.14	$5.71 \cdot 10^{-3}$	21.5	46.8	2.2
BESNO 4	Irganox® 1098	0.42	$1.71 \cdot 10^{-2}$	21.0	44.6	2.0
BESNO 6	Irganox® 1010	0.13	$5.73 \cdot 10^{-3}$	22.4	42.5	2.0
BESNO 7	Irganox® 245	0.13	$5.75 \cdot 10^{-3}$	22.5	48.0	2.1

nitrogen. The atmosphere of the cell was then switched to oxygen with a flow rate of 50 mL min^{-1}.

The same DSC apparatus was also used to determine the onset of oxidation temperature (OOT) as described by Astruc et al. [23]. The procedure was a simple ramp temperature of 10 °C min^{-1} under oxygen atmosphere from 50 to 250 °C after a 5 min isotherm at 50 °C under nitrogen. Fig. 1 depicts the determination of the Onset Oxidation Temperature (OOT) for the unaged BESNO 3 film sample. The thermogram shows a first small endotherm (T = 131 °C) which is related to a solid-solid transition [27] and the major endotherm is ascribed to the melting of the crystalline structure (T = 187 °C). OOT corresponds to the intersection of the baseline that comes after the melting peak with the slope at the inflection point of the rising oxidation exotherm.

2.3. TGA under N_2

The stabilizer volatility was studied by TGA under N_2 atmosphere using a Q50 apparatus (TA Instruments) driven by Q Series Explorer. Results were exploited using TA Analysis software. Samples made of pure stabilizer powder which was solvent casted into the TGA pan were heated up to the desired temperature and mass loss was monitored for isothermal exposures.

3. Results

3.1. Analysis of unaged samples

The OIT thermograms of the unaged film samples under study are presented in Fig. 2a (samples with an increasing Irganox® 1098 content, see composition Table 2) and 2b (samples stabilized with a

Fig. 1. Determination of the onset of oxidation temperature (OOT) for unaged BESNO 3 film sample (0.14% Irganox® 1098).

similar concentration of phenol function [AH]: Irganox® 1098, Irganox® 1010 and Irganox® 245).

Contrary to polyethylene [28−31], the thermograms of the stabilized PA11 are characterized by the absence of induction period. It seems to be a common trend with the oxidation of stabilized hexalactame [32] and PA6 [33] in which the determination of induction time is impossible for samples exposed to oxygen atmosphere [34].

In the earliest stage, the heat flow continuously increases and its changes can be decomposed into two steps. The auto-retardant shape of the thermograms is common with the shape of oxygen uptake and chemiluminescence curves for both stabilized and stabilized samples [35,36]. The exothermicity clearly decreases when the initial antioxidant content increases as observed for the maxima of curves and the pseudo inflection point. When the stabilizer weight ratio is above ca 0.1%, there is no clear trend so that the quantification of the stabilizer content from the value of the maximal heat flow release does not seem possible in a wide range of stabilizer content.

Stabilizer efficiency at molten state was alternatively characterized by onset of oxidation temperature (OOT) [12,20,21,22,23,37]. Since literature points out that sample mass loss has a first order influence on the *in situ* degradation of polymer during DSC under oxygen atmosphere [20], we paid attention to the influence of sample mass on the value of OOT in order to verify that the oxidation of samples during non-isothermal DSC measurement is not controlled by oxygen diffusion [38]. Some OOT thermograms for unaged BESNO 4 film sample (0.42% Irganox® 1098) are presented in Fig. 3.

The change in the shape of the oxidation exotherm is testimony of the existence of the control by oxygen diffusion (also named DLO for Diffusion Limited Oxidation) at high conversion degree of the degradation test. However, the Oxidation Onset Temperature OOT remains the same and is around 252.7 ± 1.5 °C. It suggests that the DLO influence has only a minor influence on OOT measurement at least as long as sample mass is lower than 6 mg which was carefully respected for the experimental results presented in this paper.

The OOT versus the nominal stabilizer concentration displays the classical quasi hyperbolic shape [31,37,39] as illustrated in Fig. 4. The overlap of data for virgin samples and for samples thermally aged at 110 °C under air (see '3.2. Analysis on aged samples') suggests the existence of a sort of master curve. Despite the differences in stabilizer molar mass and structure of the "non-reactive group", the data obtained for various AO almost overlap. This feature demonstrates a certain commonality in the physical chemistry of stabilization.

These results were completed by the analysis of the depletion rate induced by stabilizer direct volatilization.

Fig. 5 displays the results for Irganox® 245 powder exposed at 190 °C and 240 °C corresponding respectively to the temperature of OIT measurements (Fig. 2) and the OOT temperature of PA 11 + 0.13% Irganox® 245 (Fig. 4).
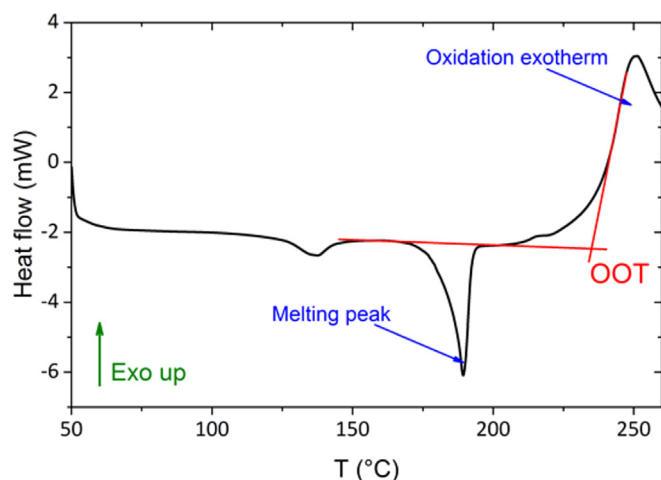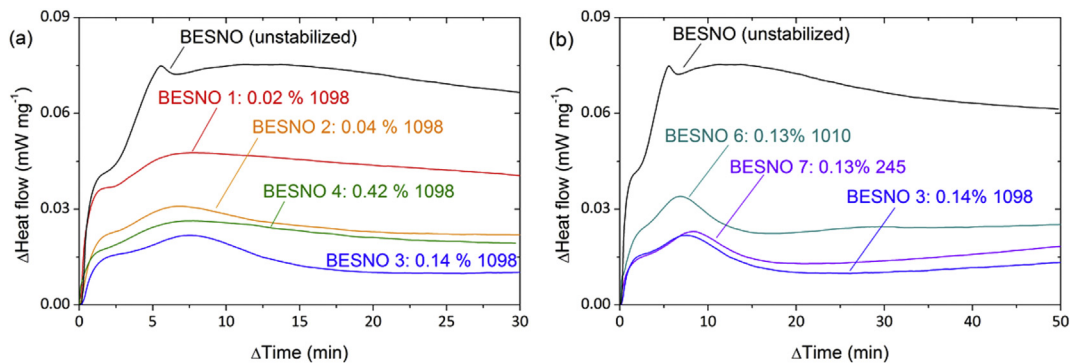
Fig. 2. OIT thermograms at 190 °C for initial film samples: Irganox® 1098 stabilized samples (a) and the influence of phenol structure (b).
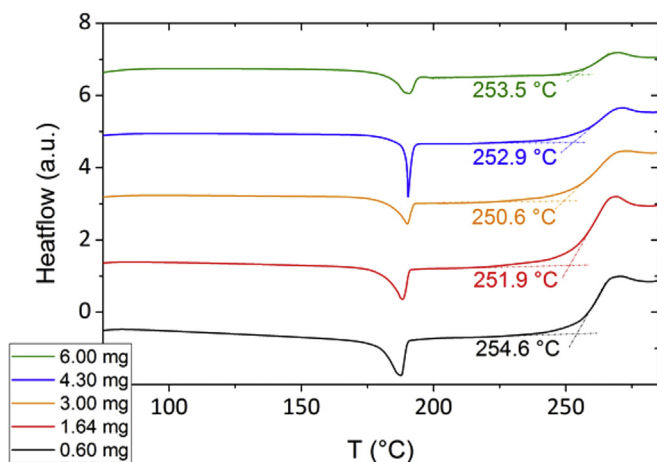

Fig. 3. OOT thermograms for an increasing mass of BESNO 4 film sample (0.42% Irganox® 1098).
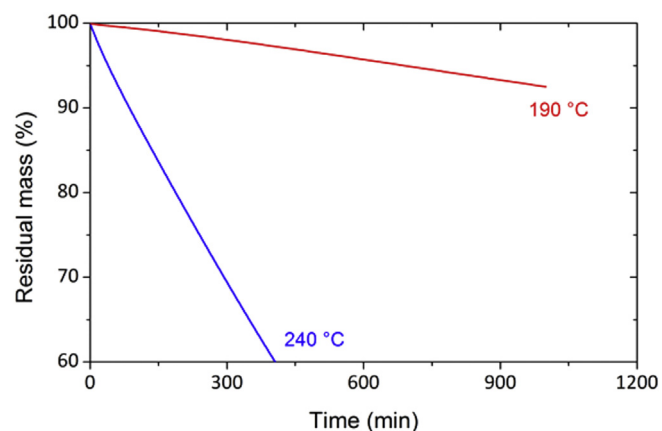

Fig. 4. Onset of Oxidation Temperatures values versus by residual antioxidant concentration (measured by HPLC measurement). NB: Data for BESNO 3 correspond to virgin and thermally aged samples at 110 °C under air, data for BESNO 2, 4,6 and 7 correspond to virgin samples.

One sees that:

- Even at 240 °C, stabilizer is not totally depleted within the first 400 min. The time for evaporating 100% of Irganox® 245 would be ca 1000 min.

Fig. 5. TGA curves of pure Irganox 245 under N_2 atmosphere.

- Depletion curves are almost linear. The rate of mass loss was converted into a volatilization constant k_{ev} [40] from:

$$\Delta m/m_0 = a.t \tag{2}$$

(a being the slope measured from Fig. 5).

$$dm/dt = a.m_0 \ \left(\text{in g s}^{-1}\right) \tag{3}$$

$$k_{ev} = a.m_0/S \ \left(\text{in g m}^{-2} \ \text{s}^{-1}\right) \tag{4}$$

where S is the TGA pan surface area.

The same experiments were conducted for the other stabilizers in a wider range of temperature. The rate of mass decrease was converted into the k_{ev} term which were plotted into an Arrhenius diagram (Fig. 6):

- Evaporation rate obeys structure-properties relationships with the following order: Irganox® 245 > Irganox® 1098 > Irganox® 1010 consistently with the molar mass values and the possible cohesive interaction in the stabilizer crystals (linked to the existence of amide groups for example in Irganox 1098.
- At high temperatures, it seems that the volatilization rate actually obeys Arrhenius law in a first approach despite a more refined mathematical description of temperature changes of volatilization rate is possible [40] and even necessary in the case of extrapolation at low temperatures. The relatively high activation energy is related to the volatilization enthalpy which is
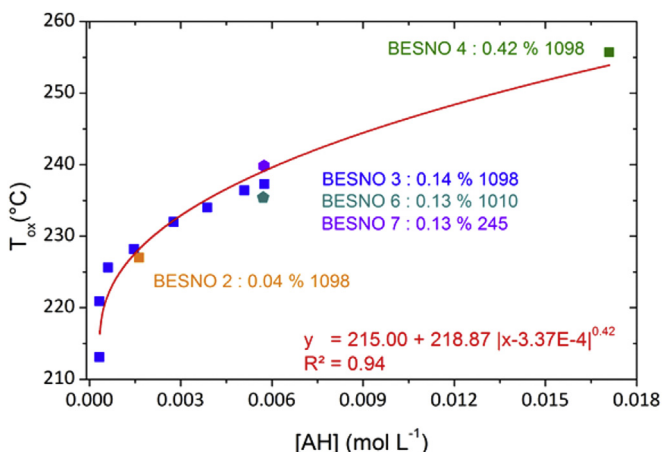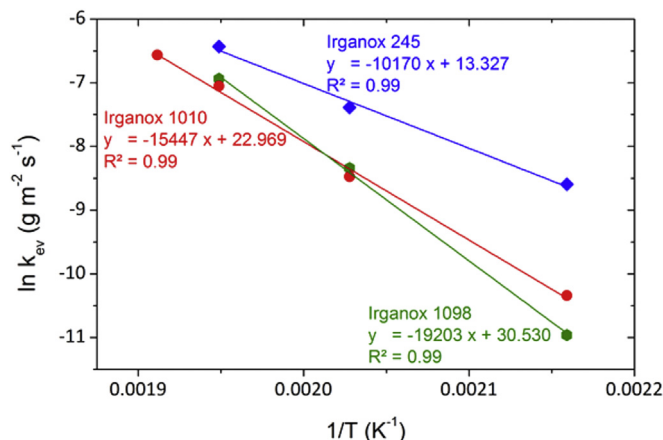
Fig. 6. Arrhenius diagram of evaporation constant of pure stabilizer: Irganox® 1098, Irganox® 1010 and Irganox® 245.
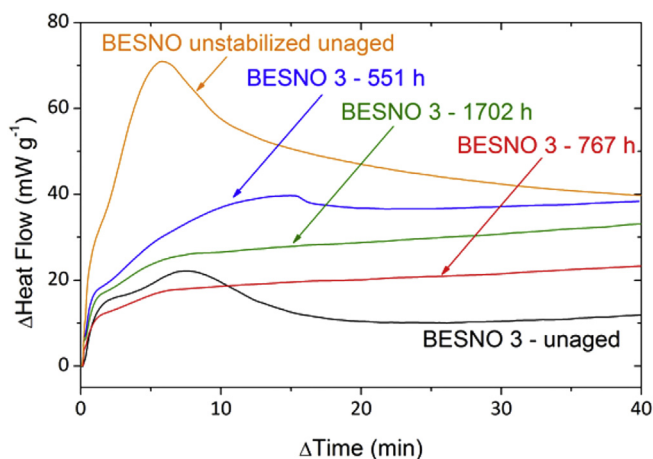
Fig. 7. OIT thermograms of stabilized PA11 samples aged under air at 110 °C (BESNO 3: PA11 + 0.14% Irganox® 1098).

expected to be high for antioxidants since it is directly linked to the cohesive energy:

$$E_{coh} = \Delta H_{vap} - RT \tag{5}$$

E_{coh} ranging from 256 to 500 kJ mol^{-1} for the stabilizers under study, according to the additive group contribution method proposed by Van Krevelen [41].

3.2. Analysis of aged samples

Some stabilized samples were aged under air at 110 °C then characterized by OIT at 190 °C (Fig. 7).

As expected, the maximal heat release level increases continuously for thermally oxidized samples, consistently with the matter that the residual concentration in hindered phenols decreases during aging. However, it was unreliable to extract the residual concentration in phenols from the experimental thermograms as the induction period is truly low [12,20].

During oxidation, OOT was found to decrease continuously and tend towards the value of the unstabilized PA11 sample. The OOT depletion curve was plotted in Fig. 8 and compared to the residual phenol concentration obtained by HPLC measurements. Both sets of data seem in good agreement suggesting that OOT could possibly be used, in a first approach, for the quantification of phenol stabilizers in thermally oxidized PA11.
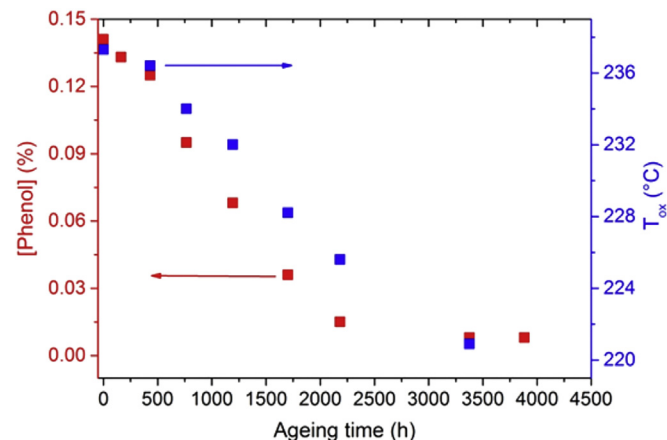

Fig. 8. OOT and residual phenol content changes versus time for PA11+ 0.14% Irganox® 1098 film samples aged at 110 °C under air.

4. Discussion

4.1. On the mechanism of stabilizer depletion

It has been reported for years that stabilizer efficiency depends:

- On its ability to scavenge the "target species" (here free POO° [42,26]).
- On its physical performances [43−46]: diffusion, solubility, evaporation …

It is hence first important to check if stabilizer is depleted by physical or chemical loss prior to interpret thermal analysis results and claim it can be used to determine stabilizer concentration. According to Calvert and Billingham [45], the rate of stabilizer depletion in a film (such as those analyzed in thermograms presented in Fig. 2) can be expressed by deriving Eq. (3):

① for a polymer film where stabilizer concentration is below its solubility limit [stab]$_{sat}$:

$$-dm/dt = k_{ev}.[stab]/[stab]_{sat} \tag{6}$$

$$-d[stab]/dt = H.[stab]/[stab]_{sat} \tag{7}$$

Where:

- e is the thickness of the considered sample (e ~ 200 μm)
- d[stab]/dt and H = k$_{ev}$/M$_{stab}$/e are expressed in mol L^{-1} s^{-1}
- k$_{ev}$ being the rate of evaporation of pure stabilizer (typically expressed in g m^{-2} s^{-1}), and deduced from Fig. 5.

It lead to:

$$[stab] = [stab]_0.exp(-H.t/[stab]_{sat} \tag{8}$$

And:

$$t_{90} = ln10^*[stab]_{sat}/H \text{ for evaporating 90\% of stabilizer} \tag{9}$$

② for a polymer film where stabilizer concentration is above its solubility limit [stab]$_{sat}$ or for pure stabilizer directly:

$$-dm/dt = k_{ev}$$

$$-d[stab]/dt = H$$

So that:

$$[stab] = [stab]_0 - H.t = [stab]_{sat} - H.t \qquad (10)$$

And:

$$t_{90} = 0.9^*[stab]_{sat}/H \text{ for evaporating 90\% of the stabilizer} \qquad (11)$$

It means that the time for evaporating stabilizer is necessarily higher in a film where stabilizer is below its solubility limit than in a film where stabilizer is higher than its solubility limit. For instance in the case of PA11 + 0. 13% Irganox® 245, stabilizer is expected to be depleted in more than 1000 min at 240 °C and more than 16000 min at 190 °C (Fig. 5).

Using the data presented in the Arrhenius diagram, the same kind of calculation can be performed for Irganox® 1010 and Irganox 1098. It was found that:

- for Irganox® 1098: $k_{ev} = 4.1 \times 10^{-3}$ g m^{-2} s^{-1} at 250 °C and 6×10^{-6} g m^{-2} s^{-1} at 190 °C.
- for Irganox® 1010: $k_{ev} = 4.0 \times 10^{-3}$ g m^{-2} s^{-1} at 250 °C and 2.5×10^{-5} g m^{-2} s^{-1} at 190 °C

On the reasonable assumption that solubility limit is systematically higher than 1% for both stabilizers in the temperature range under investigation (see "APPENDIX"), i.e. [Irganox® 1098]$_{sat}$ = 0.016 mol l^{-1} and [Irganox 1010]$_{sat}$ = 0.0085 mol l^{-1}, the characteristic time for total stabilizer evaporation can be calculated:

- for Irganox® 1098: t = 0.16 h at 250 °C and 100 h at 190 °C.
- for Irganox® 1010: t = 0.3 h at 250 °C and 48 h at 190 °C.

In other words, stabilizer physical loss is negligible during the time needed for DSC experiment according to our analysis.

4.2. On the Diffusion Limited Oxidation (DLO) effect

It is known that polymer oxidation is diffusion controlled when the rate of oxygen consumption on the edges of bulk samples is higher than its rate of diffusion. It was also found that the sample mass would play an important influence on the OIT or OOT measurement [12]. Two issues are raised:

① Are the samples aged at 110 °C subjected to DLO effects? Thickness of oxidized layer is ca 150−200 μm in pure PA66 [47], and would be higher than 1 mm in PA11 [24]. In stabilized polymers, the rate of oxygen consumption is lower than in unstabilized one. In other words, the oxidation of 70 μm thick samples of PA11 stabilized with phenols is not expected to be controlled by oxygen diffusion.
② Are the samples subject to DLO effect during OIT or OOT measurements? According to Fig. 3, it seems that OOT is shifted towards higher values when sample mass is higher than 6 mg (which experimentally correspond to the stacking of 3 PA11 foils i.e. a sample thickness ca 200 μm) which is testimony of a DLO effect above this thickness. Even if it does not change the shape of Fig. 3, we systematically analyzed samples of mass ranging from 3 to 5 mg, i.e. for which OOT measure does not depend, in a first approach, of sample mass and control by oxygen diffusion.

4.3. On the use of OIT or OOT to quantify residual stabilizer in thermally oxidized PA

It is first clear that the OIT thermograms of PA11 (and other aliphatic polyamides [48]) are different from those reported in the case of polyolefins [26,30,49]. It is tempting, in such cases, to suppose that both kinds of polymers have distinct oxidation mechanisms, however the kinetic analysis shows that the same mechanism can generate both kinetic behaviors, depending on the initiation rate value. As a matter of fact, the induction period is shortened or even disappears completely when the rate constant k_u of hydroperoxide unimolecular decomposition or the initial hydroperoxide concentration [POOH]$_0$ are increased [48]. Here, α amino hydroperoxides are destabilized by the inductive effect of the neighbouring electronegative nitrogen atom [50], the rate constant of POOH decomposition is expected to be noticeably higher than the one of polyolefin hydroperoxides, that explains, at least partially the observed difference. Since its rate constant is especially high, unimolecular POOH decomposition must be competitive with the bimolecular one and presumably predominates in the exposure conditions under study. However this characteristic is not sufficient to explain the whole kinetic behavior of PA11, especially the existence of a very fast first stage (Fig. 7) during which the stabilizers seem to be almost totally ineffective. The following explanation could be tentatively proposed: The initial POOH concentration is noticeably higher than its steady state value determined by the rate constant values at the fixed temperature of exposure [24]. Thus, oxidation begins by a period "out of equilibrium" where its rate is especially high and stabilizers are inoperative. The end of this period would correspond to the first inflection point in kinetic curves. Beyond this point, stabilizers have a significant effect.

From a practical point of view, the absence of induction limits the use of OIT for determining the residual antioxidant concentration for the induction period value. Figs. 2 and 3 suggest a correlation of the level of maximal heat release with antioxidant concentration in virgin materials. However, Fig. 7 shows that this method is not reliable for thermally aged polyamide 11.

An explanation was proposed in the case of polyethylene [26]: oxidized samples contain several unstable moieties such as radicals (P°, POO°) and peroxides (hydroperoxides POOH, dialkylperoxides POOP). Hence, the behavior of stabilized sample depends not only of residual stabilizer content (expected to continuously decrease) but also on the unstable species content (expected to vary non-monotonically). This leads to the following consequence: for a given antioxidant content, the OIT value of an oxidized and a virgin sample will differ.

However, it seems that the relationships between OOT and residual phenol content is valid for both virgin and oxidized samples which is contradictory with the above explanation. A possible interpretation is that unstable species coming from ageing are very quickly destroyed during the OOT test occurring at higher temperature than OIT one, and that their quenching does not affect significantly the residual phenol content. It remains to be verified by kinetic simulations, which is out of the scope of the present paper.

5. Conclusions

The use of polyamides in industrial applications requires adding stabilizers aimed at inhibiting the thermo-oxidative process. The determination of stabilizer depletion is needed to identify the main mechanism of stabilizer loss (exudation, evaporation, reaction with radicals) and estimate the remaining time to end of life. This paper was aimed at comparing chromatographic and thermal methods

for quantifying phenolic antioxidants in virgin and thermally oxidized polyamide 11.

In the case of three current hindered phenols (Irganox® 1010, Irganox® 1098, Irganox® 245), Oxidation Induction Time under isothermal conditions (at 190 °C) was shown to be inaccurate for phenols content higher than ca 0.1%. HPLC method is reliable for both virgin and aged samples but is time consuming (sample dissolution and filtration). Oxidation Onset Temperature gives satisfying results and displays the advantage of experimental simplicity. It seems that stabilizer volatilization during experiment and Diffusion Limited Oxidation effect does not interfere with the degradation which makes this technique helpful for a wide range of commercial aliphatic polyamides.

Acknowledgements

Appendix. On the solubility of stabilizers in polyamide 11.

The solubility limit of phenol stabilizers in PA11 has been poorly documented apart the paper by Dong and Gijsman [46]. In the frame of the additive group contribution method [41], it seems that:

- The solubility parameter of Irganox® 245, 1098 and 1010 range is from 21.7 to 22.6 MPa$^{1/2}$.
- The solubility parameter of PA11 (22.0 MPa$^{1/2}$) is intermediary between PA6 (25.4 MPa$^{1/2}$) and PE (16.1 MPa$^{1/2}$). Hence, the stabilizers under investigation are expected to be more soluble in PA11 than they are in PA6 and in PE.

According to the existing data:

- The solubility of Irganox® 1098 in PA6 is higher than 4% at 190 °C [46].
- The interaction parameter for PE-Irganox® 1010 was reported ca 3.81 at 23 °C i.e. 2.44 at 190 °C [51]. Hence the solubility of Irganox® 1010 in PE would be ln w$_{1eq}$ = -(1 + χ) i.e. w$_{1eq}$ > 3% at 190 °C and certainly higher in PA11.

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