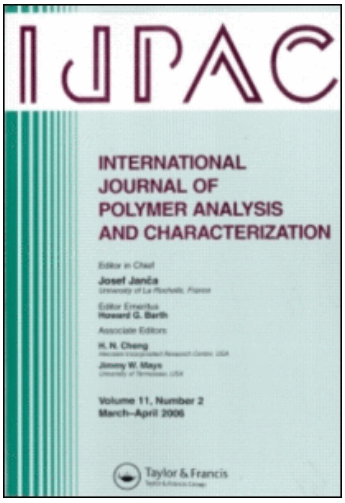

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Determination of Antioxidant Stabilizers in Polyamides via Chromatographic Separation

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Abstract: A new method for qualitative and quantitative determination of antioxidants in polyamides was developed, using the HPLC technique. The extraction of the additives was obtained by solution and precipitation of the compounds. Good repeatability was achieved for most of the antioxidants used in polyamides.

Keywords: Antioxidants; Analysis of additives; HPLC; Polyamides

INTRODUCTION

Polyamides (PAs), as the majority of polymers, are subjected to oxidative phenomena. The result of these phenomena is chain breaking and all the related changes in physical and chemical properties. Consequently, for long-life commercial applications, it is essential to use antioxidants and stabilizers in order to prevent degradation effects. The oxidative process is generally defined as a cyclical process fed by free radical reactions,[1] as shown in Figure 1. The starting point is energy absorption (heat, light) that causes the scission of the weakest covalent bonds with formation of radical species. The second step is the insertion of oxygen, yielding highly instable peroxide radicals. In order to avoid the further

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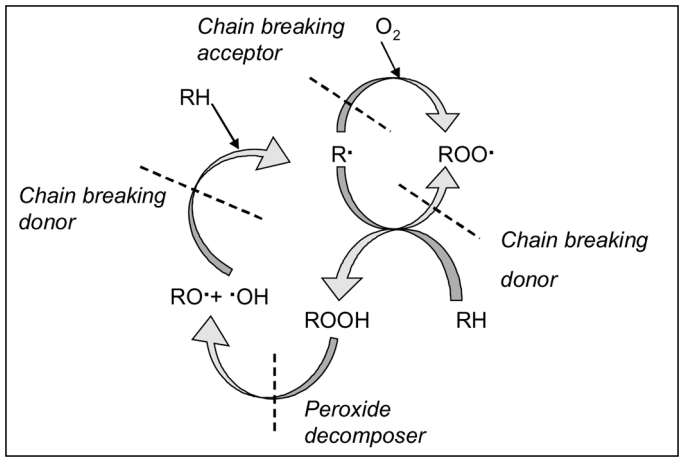

Figure 1. Typical polymer degradation cycle.

radical reactions that finally lead to chain break, it is necessary to stop this loop.

Antioxidants, or thermal stabilizers, are used to prevent degradation induced by temperature and by oxygen, for instance, during melt processing and by aging. In polyamides, the antioxidants based on hindered phenols that act as chain-breaking electron donors and radical scavengers are widely used. Another class of stabilizers are the hydroperoxide decomposers, such as the phosphites. In this case, the action on the degradation cycle is based on the possibility of reducing the peroxide and hydroperoxide reactions, transforming them to non-radical, stable products.

Stabilizers are generally introduced in polymers through a compounding process, in which the additives are mixed in the melt polymer mass, with the most homogeneous distribution possible. In some cases, this compounding process can cause some additive loss, because a chemical transformation can occur, caused by the temperature and/or mechanical stress or by a direct loss during the dosing operations. As a matter of fact, the aging properties of the polymer are directly related to the amount of antioxidant contained in the polymer. Consequently, there is a clear interest in developing analytical methods for the determination of such additives in polymers that are able first to detect qualitatively the type of stabilizers and then to quantify them precisely.

Many studies have been published in recent years on the analysis of antioxidants, most of them applied to polyolefines. A general review of published methods is reported by Jenke.[2] Recently, an inter-laboratory

test on the determination of antioxidants in polyolefines was carried out, using direct and indirect methods, and resulting in a general overview of possible techniques.[3]

A difficult point of such a type of analysis is the separation of additives from the polymer matrix. In the case of polyolefines, this step is traditionally obtained in the following ways:

- Classical Soxhlet extraction with various solvents[4]
- Dissolution of polymer and precipitation with a nonsolvent[5]
- Microwave-assisted extraction (MAE)[6]
- Supercritical fluid extraction (SFE)[7,8]

When additives are extracted from the polymer, chromatographic techniques are often used for the final characterization and quantitative determination. As a matter of fact, among the chromatographic methods, high-performance liquid chromatography (HPLC) is the most often used: the conventional reverse-phase C18, a simple gradient, and the UV detector are suitable for the separation of hindered phenols and phosphites.

In the case of polyamide, very few examples of additive extraction have been reported.[9] As a matter of fact, the separation of stabilizers from the polyamide matrix is quite difficult because of high crystallinity and strong interchain interactions, which are due to hydrogen bonding between the chains. The diffusion of small molecules through the solid matrix is very slow, and only a solvent able to swell the polyamide can be effective for extraction. Thus, the ideal solvent for classical Soxhlet extraction of additives in polyamides has to join the capacity to swell the polymer matrix to good affinity with the additive molecule; this makes the choice very limited. Even more interesting and effective extraction methods, such as MAE and SFE, have to also face a difficulty in the solvent choice when applied to polyamide matrices.

The dissolution of the polymer and further precipitation with a nonsolvent could be an efficient separation method applied to the polyamides; the advantage is that the polymer can precipitate from the solution by using a variety of solvents, chosen from among the most suitable for additive dissolution.

The scope of this work is to find a simple method for the qualitative identification and quantification of common antioxidant additives commercially used in polyamide 6 and 66. Such a method has the following steps (detailed in the experimental section):

1. Separation of additive from the polymer
2. Qualitative identification of the antioxidant
3. Quantitative determination.

EXPERIMENTAL SECTION

Sample Choice and Preparation

Table I summarizes the list of antioxidants most applied for PA stabilization, giving some information about their nature. In some cases, additives supplied by competitive companies are chemically equivalent (see Irganox 1010 and Hostanox O10); in this case, only one sample was considered. For commercial blends, the single component of the blend was considered. A common standard solution was prepared using Irganox 1010, Irgafos 168, Ultranox 626, Irganox 1098, and Hostanox O3 in a concentration of 0.5% (pure additives, supplied by the companies mentioned in Table I) mixed with PA66 powder, supplied by Rhodia EP. For analytical purposes, a series of model standard samples was also prepared using the single pure additive and PA66 powder (three different concentrations). Table II shows the list of samples prepared for this study.

The concentrations of additive corresponded to the range used in real formulations. Moreover, in order to better approach the real case, some samples were also prepared by extrusion in a pilot-plant using conditions shown in Table III.

Equipment and Solvents

For HPLC analysis a Varian PRO STAR 230 liquid chromatograph was used, equipped with a photodiode array detector (PAD). The column was an Alltech GROM Saphir 110 C18, 125 mm length, 4 mm diameter, granulometry 5 μm.

TFE solvent was supplied by Fluka. All other solvents were supplied by Carlo Erba. Internal standard benzophenone was supplied by Sigma Aldrich.

RESULTS

Separation of Additive from Polymer

The choice of a method for the separation of additives from the polyamide matrix is the focal point of the analysis. The advantages of the solution/precipitation method are clear, essentially for the possibility of using many types of solvents for the PA precipitation, because polyamides 6 and 66 are soluble in a very limited number of solvents.

For the solution of the polymer it is possible to use 2,2,2-trifluoroethanol (TFE), frequently used in the PA field as alternative to the more common PA solvents (formic and sulphuric acid, meta-cresol).

Table I. Most used antioxidants/UV-stabilizers for PA

Commercial name	Supplier	Chemical name	CAS number	Type of action
Irganox 1010 or Hostanox O10	CIBA Clariant	Pentaerythritol tetrakis (3-(3′,5′-di-tert-butyl-4′-hydroxyphenyl))	[6683-19-8]	Antioxidant–hindered phenol
Irgaphos 168	CIBA	Tris(2,4-di-tert-butyl-phenyl) phosphite	[31570-04-4]	Antioxidant–phosphite
Ultranox 626	Crompton	Bis-(2,4-di-tertbutylphenyl)-pentaerythritol diphosphite	[26741-53-7]	Antioxidant–phosphite
Irganox 1098	CIBA	N,N′-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenylpropionamide))	[23128-74-7]	Antioxidant–phosphite
Hostanox O3	Clariant	[bis-(3,3-bis-(4′-hydroxy-3′-tert-butylphenyl)butanoic acid)-glycol ester	[32509-66-3]	Antioxidant–hindered phenol
Irganox B1171	CIBA	Commercial blend of	Irganox 1098	Irgafos 168
Hostanox O310	Clariant	Commercial blend of	Hostanox O3	Hostanox O10

Table II. List of samples prepared for the study

	Name	Type of action	Model sample prepared	Extruded sample prepared
1	Irganox 1010	Antioxidant	PA66 powder + additive Concentration level of 0.1%, 0.5%, and 1%	PA66 + additive Concentration level of 0.1%, 0.5%, and 1%
2	Irgaphos 168	Antioxidant	PA66 powder + additive Concentration level of 0.1%, 0.5%, and 1%	PA66 + additive Concentration level of 0.1%, 0.5%, and 1%
3	Ultranox 626	Antioxidant	PA66 powder + additive Concentration level of 0.1%, 0.5%, and 1%	PA66 + additive Concentration level of 0.1%, 0.5%, and 1%
4	Irganox 1098	Antioxidant	PA66 powder + additive Concentration level of 0.1%, 0.5%, and 1%	PA66 + additive Concentration level of 0.1%, 0.5%, and 1%
5	Hostanox O3	Antioxidant	PA66 powder + additive Concentration level of 0.1%, 0.5%, and 1%	PA66 + additive Concentration level of 0.1%, 0.5%, and 1%
6	All antioxidants		PA66 powder + additives at points 1, 2, 3, 4, and 5 Concentration level of 0.5%	

Table III. Conditions for compound preparation

Extruder	L/D screw	Extrusion rate	Barrel temperature	Feeding point
Goetfert 015/6768 monoscrew	28	5 Kg/h	260°–285°C	First zone

Several solubility tests were carried out in order to find a suitable solvent for the efficient solution of all the antioxidants at the same time at room temperature. The chosen solvent (or mixture of solvents) has to be miscible with TFE, to have a good affinity with all the antioxidants studied, and finally has to precipitate the polyamide in the form of a thin powder, in order to allow easy filtration.

Table IV show the results of solubility tests. There is not a single suitable solvent for the solution of all antioxidants at the same time. First, a binary solution 1:1 chloroform and isopropyl alcohol was found to be effective. However, it was found that by adding a small amount of cyclohexane the quality of TFE precipitation improves; the resulting small and regular precipitated particles allow very effective filtration. As a result, the final solution was a ternary mixture: 50% chloroform, 49% isopropyl alcohol, 1% cyclohexane. Using this solution as precipitating agent, the best separation conditions were reached: the polyamide precipitated easily in powder form and the solution of antioxidant was rapid, efficient, and stable during the experiment.

The experimental details are as follows:

- 2 g of polymer were dissolved in 25 mL of TFE, heating until the complete dissolution of the polyamide

Table IV. Solubility test, carried out at room temperature

	Irganox 1010	Irgafos 168	Ultranox 626	Irganox 1098	Hostanox O3
Acetonitrile	Yes	No	No	No	Yes
Acetone	Yes	No	No	No	Yes
Chloroform	Yes	Yes	No	Yes	No
Methanol	No	No	No	No	Yes
Ethyl acetate	Yes	No	No	No	No
Isopropanol	No	No	Yes	Yes	Yes
Cyclohexane	Yes	Yes	Yes	No	Yes
TFE	No	No	No	No	No
Mix: 50% chloroform, 50% isopropanol	Yes	Yes	Yes	Yes	Yes

- 200 mL of the ternary solution chloroform/isopropyl alcohol/cyclohexane were added, and the polymer precipitated as a white powder
- After few minutes the solution was filtered with a glass sintered filter (porosity 20–40 μm), and the precipitate washed with fresh ternary solution
- The solution was dried, and 5 mL of ternary solution containing the internal standard (benzophenone in concentration of 1.1% w/v) was added to the residual.

This final solution was then ready for injection in the HPLC column.

Conditions of HPLC Separation

For antioxidant separation by HPLC a ternary gradient was used, starting with 20% water : 15% ethylacetate : 65% methanol, arriving at 100% ethylacetate in 15 min. The flow rate was 1.5 mL/min, the injection volume was 5 μL, and the oven temperature was 30°C. The UV detector PAD was focused on 275 nm. Benzophenone in the concentration of 1.1% w/v was used as internal standard for all quantitative tests.

Qualitative Determination of Additives

Figure 2 shows the resulting chromatogram of the five antioxidants of a standard model sample containing all antioxidants at the same time at

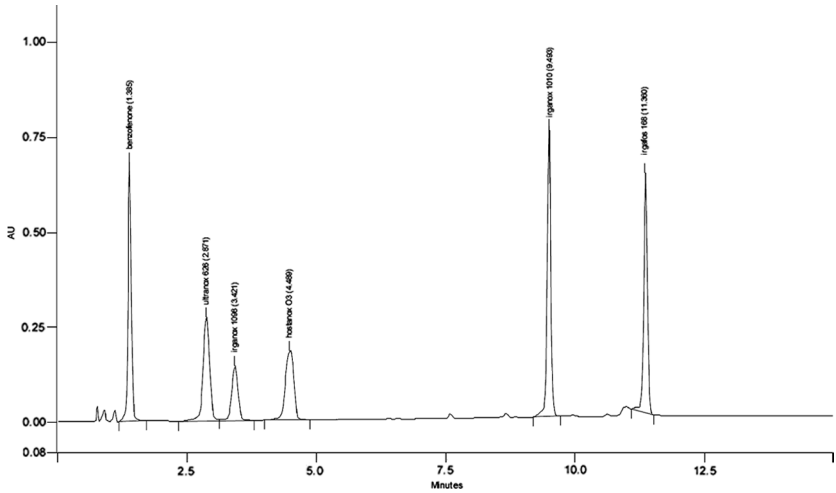

Figure 2. HPLC chromatogram of antioxidant additives (from model standard samples).

Table V. Retention times in HPLC chromatogram for antioxidants

Antioxidant	Retention time (min)
Irganox 1010	9.5
Irgaphos 168	11.4
Ultranox 626	2.9
Irganox 1098	3.4
Hostanox O3	4.5

a concentration of 0.5%. Table V shows the corresponding retention times; all peaks are well separated. The polyamide base, following the sample preparation described above, does not produce any interference in such conditions (for instance, there are not traces of oligomers in the HPLC chromatogram).

Quantitative Determination of Additives

In the case of quantitative determination, a calibration curve was established for each antioxidant. In Figure 3 the HPLC calibration curves are reported for the antioxidants studied.

In order to confirm the good results obtained with model samples, the same method was applied to extruded compounds. In the case of Ultranox 626, the three different levels of additive in the compound were correctly detected by HPLC (see Figure 4). Similar results were obtained with Irganox 1098, Hostanox O3, and Irgafos 168. The data of standard

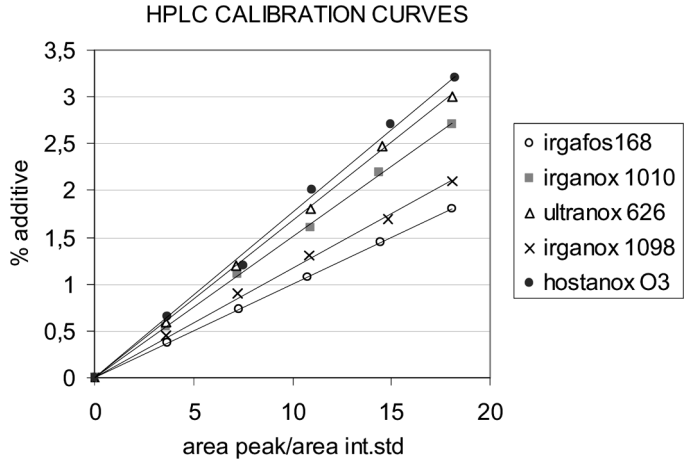

Figure 3. HPLC calibration curves for some antioxidants.

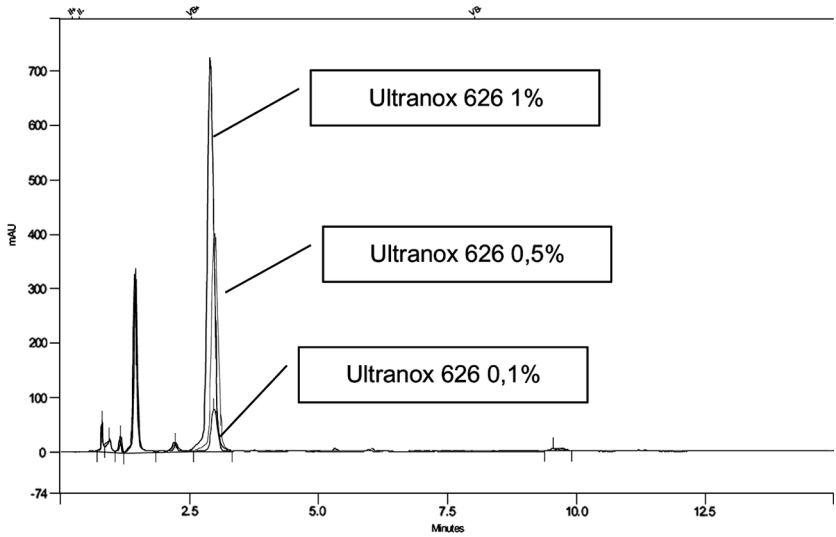

Figure 4. Superposed chromatograms of three extruded compounds containing Ultranox 626 at 0.1, 0.5, and 1% of concentrations.

deviations obtained in the tests (referring to a concentration of 0.5%) are reported in Table VI.

However, in the case of Irganox 1010, the extrusion process caused some additional modification. In Figure 5, Irganox 1010 (or Hostanox O10) is no longer present in the chromatogram, and other unidentified peaks appear. In the past, the stability of this additive was often studied in polyethylene and polypropylene applications;[10,11] fragmentation caused by the hydrolysis and thermal degradation was proposed on the basis of model hydrolysis experiments.[11] It is possible to attribute these peaks to fragmentation of the antioxidant during the compounding process. As result, it is obvious that a quantitative analysis for such a type of antioxidant becomes difficult.

Table VI. Repeatability data (standard deviation calculated on the basis of multiple tests on the same sample). Sample at 0.5% of additive

Antioxidant	No. of tests	Average	Std. deviation
Irganox 1010 (concentration 0.5%)	10	—	—
Irgaphos 168 (concentration 0.5%)	10	0.56%	0.046
Ultranox 626 (concentration 0.5%)	10	0.53%	0.023
Irganox 1098 (concentration 0.5%)	10	0.55%	0.034
Hostanox O3 (concentration 0.5%)	10	0.48%	0.035

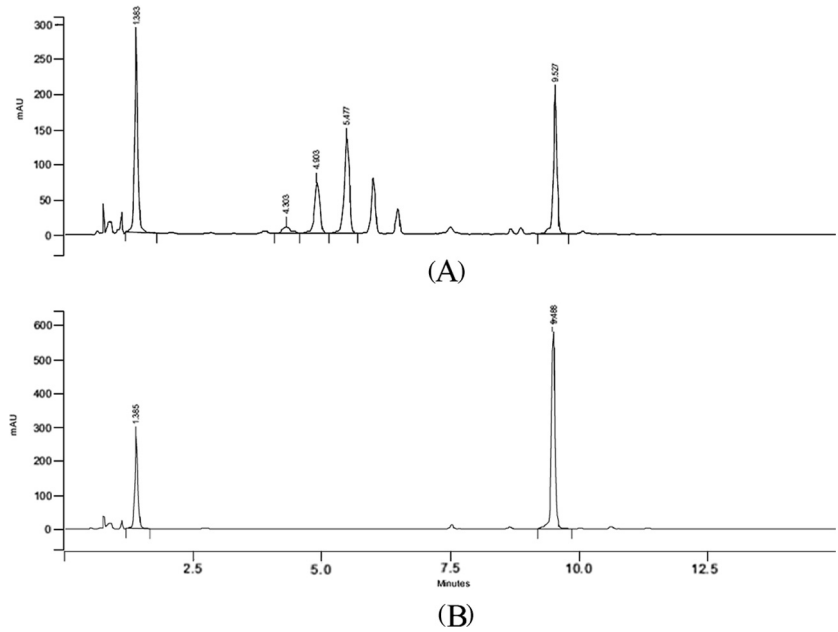

Figure 5. HPLC chromatogram of Irganox 1010 (0.5% concentration): A, Irganox 1010 separated by the compound; B, Irganox 1010 separated by model sample.

CONCLUSION

The proposed method is suitable for identification of the most frequently used antioxidants in polyamides. The sample preparation described here allows one to analyze the unknown compositions in just one step, the same for all the antioxidants. The qualitative identification of antioxidant molecules is clear and not affected by the interferences.

The quantification of the additives is also possible for most of them, with the exception of Irganox 1010. As a matter of fact, Irganox 1010 shows some fragmentation phenomena that make a clear quantitative determination impossible.

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