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Polymer additive analysis by pyrolysis–gas chromatography IV. Antioxidants

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Abstract

Antioxidants are important additives in polymers. Because of the low level of antioxidants normally used, they cannot be analyzed directly by common spectroscopic or thermal chemical techniques. However, antioxidants as well as other additives in polymers can be qualitatively analyzed by pyrolysis–gas chromatography (Py–GC) after separating the polymers and additives. In this study, several antioxidants have been investigated to demonstrate that Py–GC is a viable tool to analyze them. The advantages of using Py–GC in the analysis of antioxidants have also been discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Polymers; Antioxidants

1. Introduction

Inherently, all polymeric materials will react with oxygen. The kinetics of the oxidation reaction depend on the type of polymers as well as the processing and application environment, such as temperature, humidity, etc. The oxidation reaction is present in every stage of the life cycle of a polymer such as synthesis/manufacture, processing (extrusion, molding, etc.), and final application usage by the customers [1]. It is necessary to prevent or slow down this oxidation activity in order to extend the use of the polymer.

The typical oxidation phenomena are generalized in terms of “degradation” or “aging”. The results of oxidation reactions are seen as discoloration (yellowing), loss of gloss or transparency, chalking and

surface cracks. On the other hand, the result of the oxidation reaction occurs more or less simultaneously as loss of mechanical properties such as impact strength, elongation, tensile strength, etc. The phenomenon of oxidation reaction also accounts for the occurrence of two degradation processes, chain scission and cross-linking. Chain scission results in the loss of molecular mass, increase in melt flow, and decrease in toughness. Cross-linking increases molecular mass, decreases melt flow and increases toughness in the early stage.

Fundamentally, there are several different approaches to reduce the speed of or prevent the oxidation reaction. For example, the oxidation reaction can be slowed by structural modification of the polymer through copolymerization with monomers that have antioxidation capability. The second way to decrease the effect of the oxidation reaction is to introduce inert compounds to cap off the reactive sites (normally, at the end of the chain) of the

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polymer. The third way to control the oxidation reaction is to physically stabilize the polymer by orientation of the polymer such as stretching. The final way to manage the oxidation reaction is to add stabilizing additives, such as antioxidants [2].

Addition of antioxidants seems to be the most convenient way to retard the oxidation reaction in the polymer. However, making the proper selection of an antioxidant system can be a tough task. There are an almost unlimited number of antioxidants, antioxidant combinations, and various antioxidant concentrations that might provide the required antioxidant protection. However, the criteria of choice can be as follows, (1) safety, (2) physical form, (3) volatility, (4) extractability and migration, (5) color, (6) odor and taste, (7) compatibility and (8) cost and performance [3].

Antioxidants can be divided into two major classes based on their mechanisms of action: primary antioxidants and secondary antioxidants [4]. Primary antioxidants are radical scavengers or hydrogen donors or chain reaction breakers. The major molecules of primary antioxidants include hindered phenols and secondary aryl amines. Secondary antioxidants are peroxide decomposers. They are composed of organophosphites and thioesters.

It is hard to see that a single antioxidant can provide all of the varied properties required in a polymer application. Consequently, combinations of primary and secondary antioxidants are used to take the advantage of synergistic effects [5]. A hindered phenol might be used synergistically in conjunction with a thioester where the phenol provides the long-term stability of the polymer and the thioester supplies the long-term stability for the hindered phenol. In the same way, a hindered phenol might be used in combination with a phosphite to improve color and at the same time to provide the processibility.

The concentration of antioxidants used in polymers is usually between 100 and 1000 ppm of each primary and secondary antioxidant depending on the targeted applications and the processing conditions. The spectroscopic approach to analyze antioxidant in the polymer is difficult because of ultra low concentration and interference of the parent polymer matrix. The general approach of antioxidant analysis is first to separate the polymer and additives [6],

followed by appropriate gas chromatography (GC) or liquid chromatography (LC) methods to separate and identify the antioxidants from the additive mixture. However, for the primary antioxidants such as hindered phenols, not only are these rather large molecules but also they are similar in structure. The choice of GC or LC to achieve the separation and detection/identification is laborious when facing an unknown. It always requires some application knowledge and a library of standard spectra in order to induce the correct identification. However, there is another technique, pyrolysis (Py)–GC, that may be applied to simplify this antioxidant analysis task.

Py–GC [7] is an important technique for polymer as well as large molecule analysis. Py–GC is a technique that uses thermal energy (pyrolysis) to break down a polymeric chain or large molecule to monomers, oligomers and other fragments, followed by the separation of the pyrolysates with GC and detection with appropriate detectors. Flame ionization detection (FID) is one of the most frequently used detection methods for quantitative analysis of pyrolysates. Mass spectrometry (MS) is one of the most commonly used detection methods for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain compositional data [8]. The oligomers or oligomer-related fragments are used to elucidate microstructure as well as compositional information [9]. Py–GC has been used in the antioxidant characterization for the polymer analysis, such as Irganox 1010 in polyethylene (PE) and poly(butylene terephthalate) (PBT) in the presence of tetramethylammonium hydroxide (TMAH) [10]. There is another Py–GC paper for additives in rubbers and plastics study based on the comparison of the pyrolysate's mass spectrum with an additive spectrum library [11].

Direct analysis of antioxidants in the polymer by Py–GC is difficult because of the low concentration of antioxidant and the possible pyrolysates interference from the original polymer matrix. Antioxidants as well as other additives in the polymer can be qualitatively and quantitatively analyzed by Py–GC after separating the polymer and additives. In this study, several different types of antioxidants have been studied to demonstrate that Py–GC is a good tool to investigate the antioxidants in polymers. The discussion of how to identify different antioxidants

will focus on the antioxidants with slight differences in structure. The major purpose of this approach is to demonstrate that different pyrolysates are created from different antioxidants with similar structures in order to lead to a systematic approach to identify each individual antioxidant. The advantages of using Py-GC for antioxidant analysis are also discussed.

2. Experimental

2.1. Antioxidants

Irganox 1010 (CAS No. 6683-19-8), Irganox 1076 (CAS No. 2082-79-3), Irganox 1035 (CAS No. 41484-35-9), Irganox MD1024 (CAS No. 32687-78-8), Irganox 259 (CAS No. 35074-77-2), Irganox 3114 (CAS No. 27676-62-6), Irganox 1425 (CAS No. 65140-91-2), Irganox 565 (CAS No. 991-84-4) and Irgafos 168 (CAS No. 31570-04-4) were obtained from Ciba-Geigy (Tarrytown, NY, USA). A GE Cyloloy C3600 thermoplastic resin was obtained from GE Plastic (Detroit, MI, USA). All antioxidants

and thermoplastic resin were used as they were received without any further purification.

2.2. Py-GC conditions

Samples of antioxidant (approximately 0.5 mg) were carefully deposited into a quartz tube. The quartz tube was inserted into a 300°C interface connected to the injection port of a Hewlett-Packard (HP) Model 6890 gas chromatograph equipped with an FID system. The samples were pyrolyzed (CDS 2000 Pyroprobe, Pt coil) at a calibrated temperature of 950°C. The coil was heated to the calibrated temperature at 20°C/ms and held at the set temperature for a 20-s interval. The pyrolysates were split in the 300°C injection port, with 250:1 split ratio. The GC system was set up with a fast flow program [15 p.s.i. (1 p.s.i.=6894.46 Pa)/0.2 min, 75 p.s.i./min, to 90 p.s.i./8.8 min]. The separation was carried out on a fused-silica capillary column (J & W Scientific DB-5, 10 m×0.10 mm I.D., 0.4 µm film) using a fast temperature ramping program (50°C/0.2 min, 100°C/min, to 100°C/0 min; 80°C/min, to 140°C/0

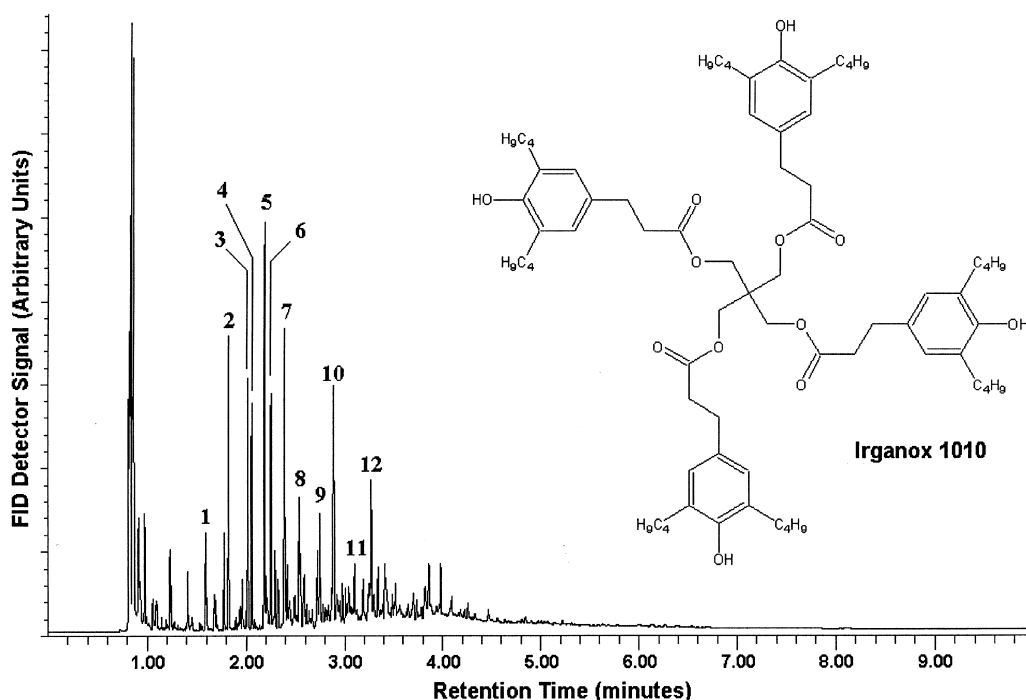


Fig. 1. The pyrogram of Irganox 1010 and its structure. The peaks labeled in the pyrogram have been identified and listed in Table 1.

Table 1
Peak assignments for the pyrograms of Irganox 1010 (Fig. 1)

Peak No.	M_r	Structure
1	94	Phenol
2	108	4-Methylphenol
3	122	2,4-Dimethylphenol
4	122	4-Ethylphenol
5	120	2,3-Dihydrobenzofuran
6	136	4-Ethyl-2-methylphenol
7	134	4-Vinyl-2-methylphenol
8	164	2- <i>tert.</i> -Butyl-4-methylphenol
9	178	2- <i>tert.</i> -Butyl-4-ethylphenol
10	218	2,6-Bis(<i>tert.</i> -butyl)-4-methylenecyclohexa-2,5-dien-1-one
11	234	2,6-Bis(<i>tert.</i> -butyl)-4-ethylphenol
12	232	2,6-Bis(<i>tert.</i> -butyl)-4-vinylphenol

min; 60°C/min, to 200°C/0 min; 50°C/min, to 280°C/0 min; 40°C/min, to 320°C/5.2 min).

2.3. Py-GC-MS conditions

The sample preparation and pyrolysis in the Py-GC-MS experiments were the same as in the Py-

GC experiments. The GC system used was a HP Model 5890 gas chromatograph. The pyrolysis products were split in the 300°C injection port, with 10 p.s.i. head pressure, and 30:1 split ratio. The pyrolysates were separated on a fused-silica capillary column (J & W Scientific DB-5, 30 m×0.25 mm I.D., 1.0 μm film) using a linear temperature pro-

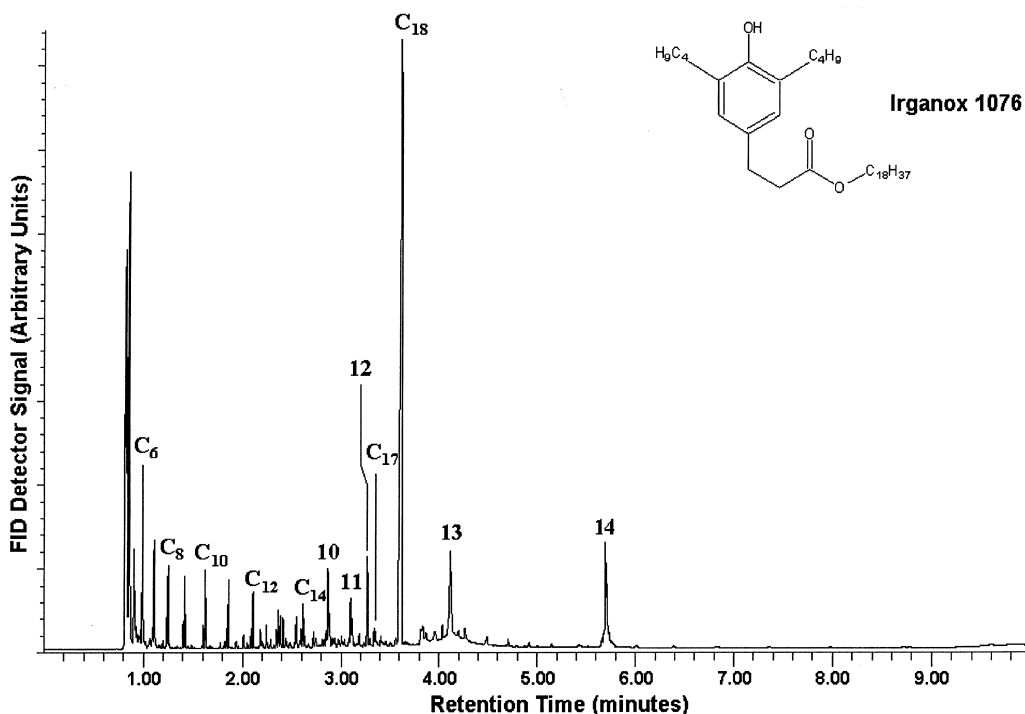


Fig. 2. The pyrogram of Irganox 1076 and its structure. The peaks labeled in the pyrogram have been identified as (13) 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoic acid, (14) Irganox 1076.

gram (40°C/4 min, 10°C/min, to 320°C/18 min); and detected by a HP 5791 mass-selective detector. The GC transfer line to the mass-selective detector was kept at 300°C. An electron ionization mass spectrum was obtained every second over the m/z range of 15 to 650. The results of Py-GC-MS were used mainly for identification of pyrolysates.

3. Results and discussion

The primary antioxidants are the family of hindered phenols and the secondary aryl amines. In the hindered phenol family, all the antioxidants are relatively similar in structure. During the identification, it is easy to conclude that a hindered phenol is used as antioxidant based on the several alkyl substituted phenol pyrolysates detected. It is hard to distinguish which specific hindered phenol related antioxidant has been used. However, if a special fragment can be found that correlated to a specific hindered phenol structure, the positive identification

still can be reached. This type of identification requires a good pyrolysis database of antioxidants as well as good pyrogram interpretation skill.

The most typical antioxidant to illustrate the hindered phenol functions is Irganox 1010. Further examination of this structure shows that it is methane with four hydrogens substituted by four hindered phenol units; the hindered phenol unit is a 3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate. Essentially, it is a phenol unit with two *tert*-butyl groups attached at positions 2 and 6, position 4 being connected to the carbon at position 3 of a propanoate. Fig. 1 shows the pyrogram of Irganox 1010 with its chemical structure. The major pyrolysates labeled in the pyrogram have been identified and are listed in Table 1. All the pyrolysates are contributed from the side chain fragmentation of hindered phenol unit. The pyrogram of Irganox 1010 can almost be viewed as the pyrogram of hindered phenol (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) unit. There is no quick/easy way to identify this antioxidant by Py-GC. If all necessary pyrolysates from hindered phenols are

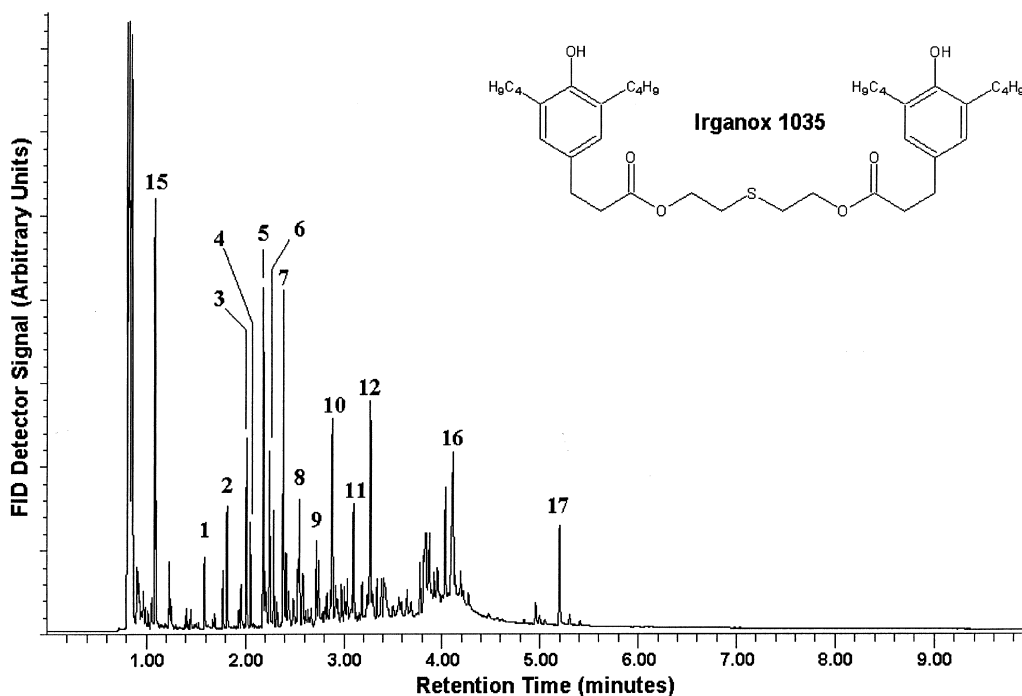


Fig. 3. The pyrogram of Irganox 1035 and its structure. The peaks labeled in the pyrogram have been identified as (15) divinyl sulfide, (16) 2,6-bis(*tert*-butyl)-4-[2-(1,3-dioxolen-2-yl)ethyl] phenol, (17) 2-vinylthioethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenol)propanoate.

present, and in the mean time there is no other special pyrolysate, the antioxidant used is probably Irganox 1010.

An antioxidant that has been widely used in thermoplastics is Irganox 1076. Fig. 2 shows a pyrogram of Irganox 1076 with its chemical structure. This antioxidant contains a hindered phenol unit with a long-chain aliphatic hydrocarbon. Several pyrolysates have been labeled in the pyrogram to show their origins either from an octadecyl aliphatic hydrocarbon chain or from a hindered phenol unit. The positive identification of this antioxidant can rely on its unique octadecyl peak and its hindered phenol related pyrolysates such as 2,6-bis(*tert.*-butyl)-4-methylenecyclohexa-2,5-dien-1-one (M_r 218), 2,6-bis(*tert.*-butyl)-4-ethylphenol (M_r 234), 2,6-bis(*tert.*-butyl)-4-vinylphenol (M_r 232), and 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoic acid (M_r 278). However, GC can analyze Irganox 1076 (M_r 530.8) directly without pyrolysis because of its thermal stability and relative low boiling point. Occasionally, even in the pyrolysis experiment, there

are vaporized (unpyrolyzed) compounds (shown in the pyrogram as peak 14 in Fig. 2).

Fig. 3 shows a pyrogram of Irganox 1035 with its chemical structure. It is a structure with two hindered phenol units connected with a thiodiethylene unit. The hindered phenol related pyrolysates indicate the presence of hindered phenol units. In addition to those, there are several pyrolysates that reflect the existence of the thiodiethylene unit. The divinyl sulfide (M_r 86) pyrolysate demonstrates the essential structure of this linking unit; the 2-vinylthioethyl 3-[3,5 di-*tert.*-butyl-4-hydroxyphenyl]propanoate (M_r 364) confirms the linkage between the hindered phenol unit with this thiodiethylene unit. The positive identification of this antioxidant depends on these two unique pyrolysates along with other typical hindered phenol pyrolysates.

Fig. 4 shows a pyrogram of Irganox 259 with its chemical structure. This compound has a structure with two hindered phenol units connected with a hexamethylene unit. The bonding between the hindered phenol and hexamethylene unit is ester bonds.

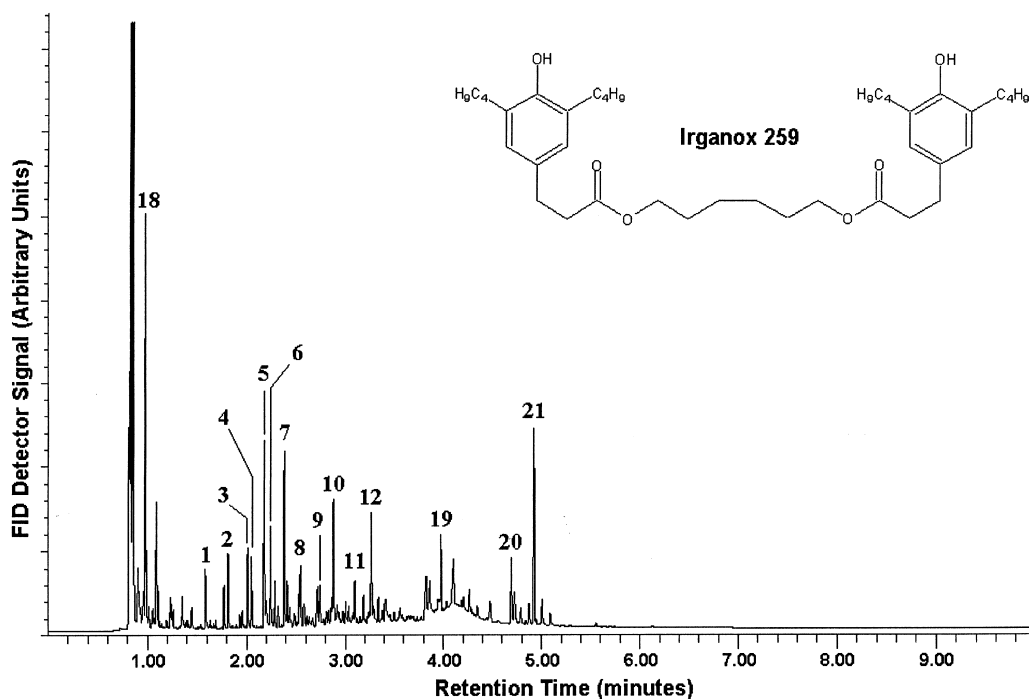


Fig. 4. The pyrogram of Irganox 259 and its structure. The peaks labeled in the pyrogram have been identified and listed in Table 1. In addition, the other peaks are (18) 1,5-hexdiene, (19) methyl 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate, (20) vinyl 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate, (21) hex-5-enyl 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate.

Similar to previous antioxidants, the pyrogram contains all hindered phenol related pyrolysates plus others that consist of hexamethylene functions. The pyrolysates such as 1,5-hexdiene (M_r 82), methyl 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate (M_r 292), vinyl 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate (M_r 304), and hex-5-enyl-3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate (M_r 360) supply the proof of the ester-type connection between hindered phenol and the hexamethylene unit. The pyrolysates, 1,5-hexdiene, and hex-5-enyl 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanoate are the best indicators to suggest the existence of this antioxidant.

Fig. 5 shows a pyrogram of Irganox MD1024 with its chemical structure. This compound has a structure with two hindered phenol units connected with a hydrazine unit. However, it is an amide bonding instead of ester bonding between the hindered phenol and connection unit. Similar to previous antioxidants, the pyrogram contains all hindered phenol related

pyrolysates plus others that consist of amide functions. The pyrolysates such as 6,8-bis(*tert.*-butyl)-7-hydroxy-1,3,4-trihydroquinolin-2-one (M_r 275), 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanenitrile (M_r 259), and 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanamide (M_r 277) provide clear evidence of amide-type connections between hindered phenols and the hydrazine unit. The pyrolysates, 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanenitrile, and 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propionate can be used to distinguish this antioxidant among others.

Fig. 6 is a pyrogram of Irganox 3114 and its structure. It contains three identical parts; each of them contains a hindered phenol unit and an isocyanate unit. These three identical units connect to each other with an isocyanate unit to form an isocyanurate ring. Because the chemical structure of the hindered phenol unit is not exactly the same as the hindered phenol mentioned previously, the pyrolysates produced from this antioxidant are slightly different. The unique set of pyrolysates from this

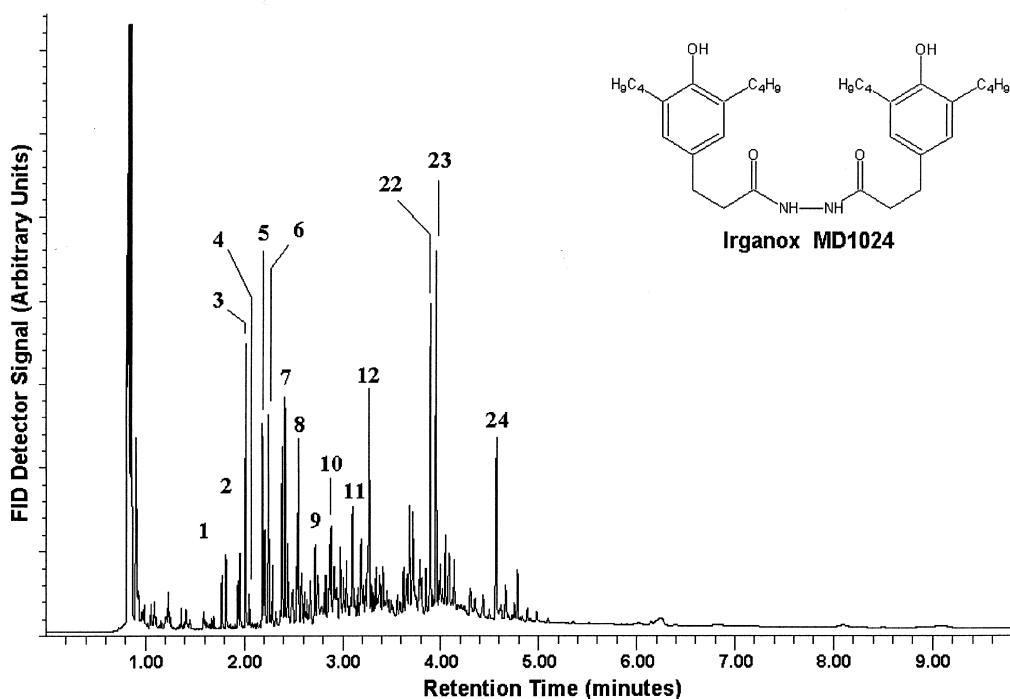


Fig. 5. The pyrogram of Irganox MD1024 and its structure. The peaks labeled in the pyrogram have been identified as (22) 6,8-bis(*tert.*-butyl)-7-hydroxy-1,3,4-trihydroquinolin-2-one, (23) 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanenitrile, (24) 3-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]propanamide.

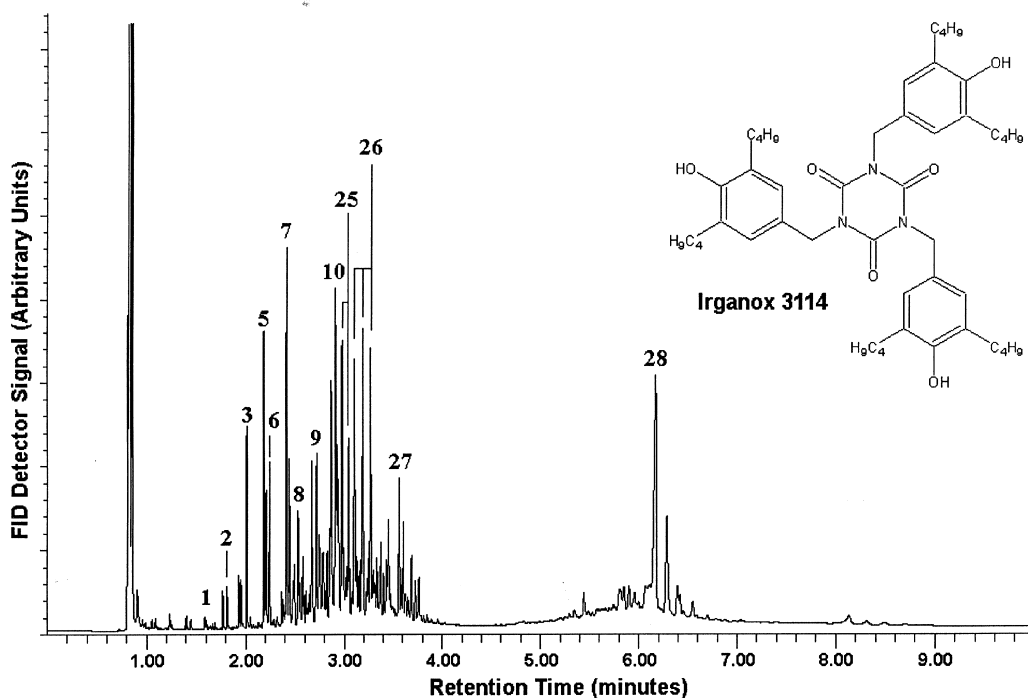


Fig. 6. The pyrogram of Irganox 3114 and its structure. The peaks labeled in the pyrogram have been identified and listed in Table 1. In addition, the other peaks are (25) isomers of 2,6-bis(*tert.*-butyl)-4-methylphenol, (26) isomers of 4-(aminomethyl)-2,6-bis(*tert.*-butyl)phenol, (27) 6,8-bis(*tert.*-butyl)-1,2,3,4-tetrahydroquinazolin-7-ol, (28) 2,6-bis(*tert.*-butyl)-4-[2-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]ethyl]phenol.

antioxidant include isomers of 2,6-bis(*tert.*-butyl)-4-methylphenol (M_r 220), isomers of 4-(aminomethyl)-2,6-bis(*tert.*-butyl)phenol (M_r 234), 6,8-bis(*tert.*-butyl)-1,2,3,4-tetrahydroquinazolin-7-ol (M_r 262), and 2,6-bis(*tert.*-butyl)-4-[2-[3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]ethyl]phenol (M_r 438). The existence of these pyrolysates indicates the structure of hindered phenol unit as well as the possible whole structure of this antioxidant. The positive identification of the existence of this antioxidant depends on the detection of these pyrolysates.

Fig. 7 is a pyrogram of Irganox 1425 and its structure. Irganox 1425 is a phosphorous-containing secondary antioxidant. It exists in the ionic form. It is a calcium salt. The organic portion contains only one hindered phenol unit with ethyl phosphonate. The numbers of different pyrolysates produced from this antioxidant are less than the others discussed. The positive identification of this antioxidant depends on unique pyrolysate produced from organic portion structure which is {[3,5-bis(*tert.*-butyl)-4-hy-

droxyphenyl] methyl}diethoxyphosphino-1-one (M_r 356).

As mentioned in the Introduction, combinations of primary and secondary antioxidants are used to take advantage of synergistic effects. Antioxidant packages such as blends of Irganox 1076 with Irgafos 168, and Irganox 1010 with Irgafos 12, are commonly used in the polymer. It is clear that the analysis and identification of secondary antioxidants are also important.

One of the most commonly used secondary antioxidants is Irgafos 168. Fig. 8 shows a pyrogram of Irgafos 168 and its structure. Irgafos 168 is a phosphite connected with three hindered phenol units in the phenol functional group. The pyrolysates of Irgafos 168 have been identified and listed in Table 2. Essentially, the hindered phenol unit produces two sets of pyrolysates, one set contains all alkyl-substituted benzenes, and the other set contains all alkyl-substituted phenols. Because the connection point differs in the hindered phenol unit, the pyrolysis

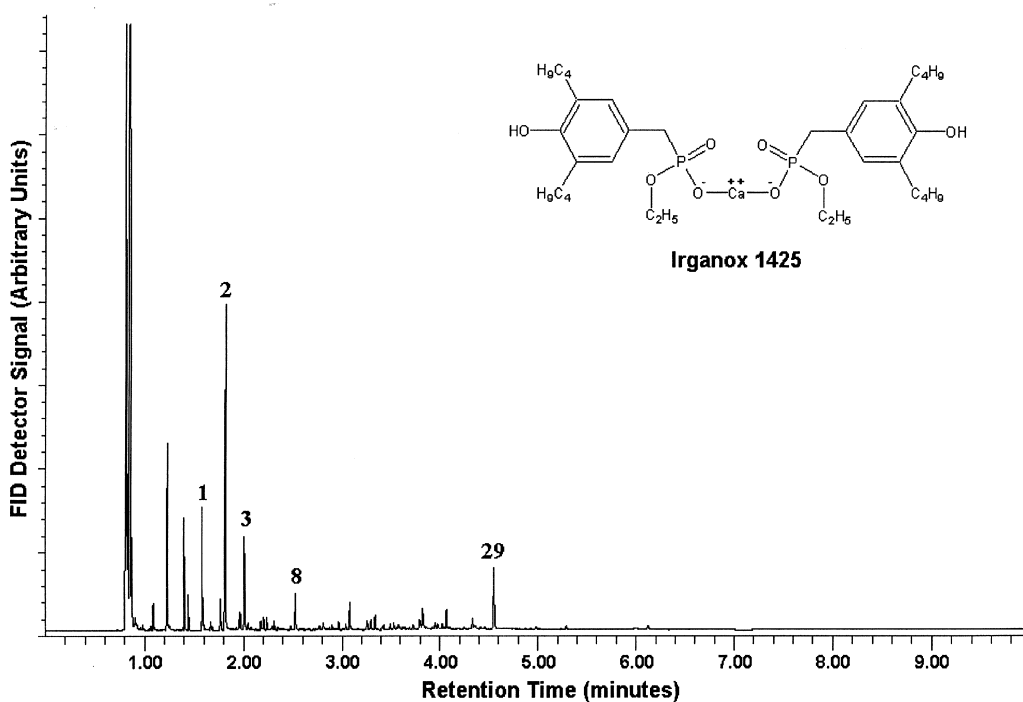


Fig. 7. The pyrogram of Irganox 1425 and its structure. The peaks labeled in the pyrogram have been identified and listed in Table 1. In addition, the other peaks are (29) [3,5-bis(*tert.*-butyl)-4-hydroxyphenyl]methyl]diethoxyphosphino-1-one.

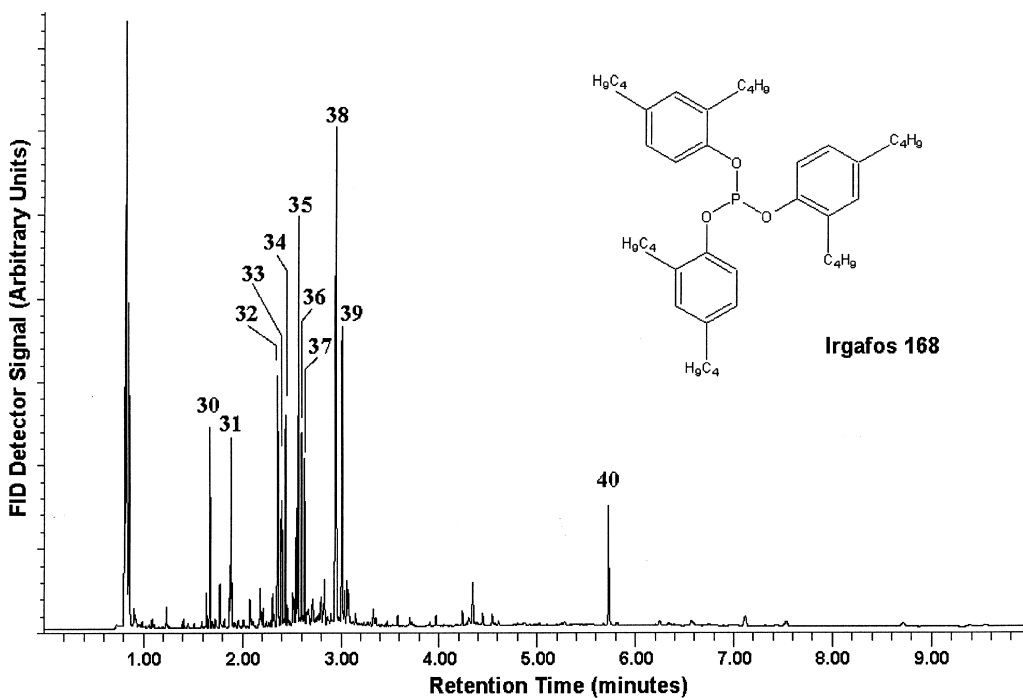


Fig. 8. The pyrogram of Irgafos 168 and its structure. The peaks labeled in the pyrogram have been identified and listed in Table 2.

Table 2
Peak assignments for the pyrograms of Irgafos 168 (Fig. 8)

Peak No.	M_r	Structure
30	134	<i>tert.</i> -Butyl benzene
31	148	3- <i>tert.</i> -Butyl toluene
32	174	1,3-Di- <i>tert.</i> -butyl benzene
33	190	1,3-Di- <i>tert.</i> -butyl toluene
34	188	1,1,4,4-Tetramethyl-1,2,3,4-tetrahydronaphthalene
35	164	2-(<i>tert.</i> -Butyl)-4-methylphenol
36	148	3,3-Dimethyl-2,3-dihydrobenzo[<i>b</i>]furan
37	188	3,3-Dimethyl-5-(1-methylvinyl)-dihydrobenzo[<i>b</i>]furan-2,3
38	206	2,4-Di- <i>tert.</i> -butylphenol
39	206	2,6-Di- <i>tert.</i> -butylphenol
40	647	Irgafos 168

pattern produced from Irgafos 168 is different from other antioxidants previously discussed. This can be attributed to the structural difference causing the change of thermal degradation pathways. The boiling point of Irgafos 168 is low enough that GC can elute the parent compound. Occasionally, the parent compound can be seen at the end of pyrogram due to vaporization in the pyrolysis interface before py-

rolyzed. The positive identification of the Irgafos 168 relies on the detection of two sets of pyrolysates plus the parent compound.

Fig. 9 shows a pyrogram of Irganox 565 and its structure. Irganox 565 is a hindered phenol unit connected to a triazine ring with two octylthiol branches. The pyrolysates of Irganox 565 are dominated by the fragmentation of the octylthiol func-

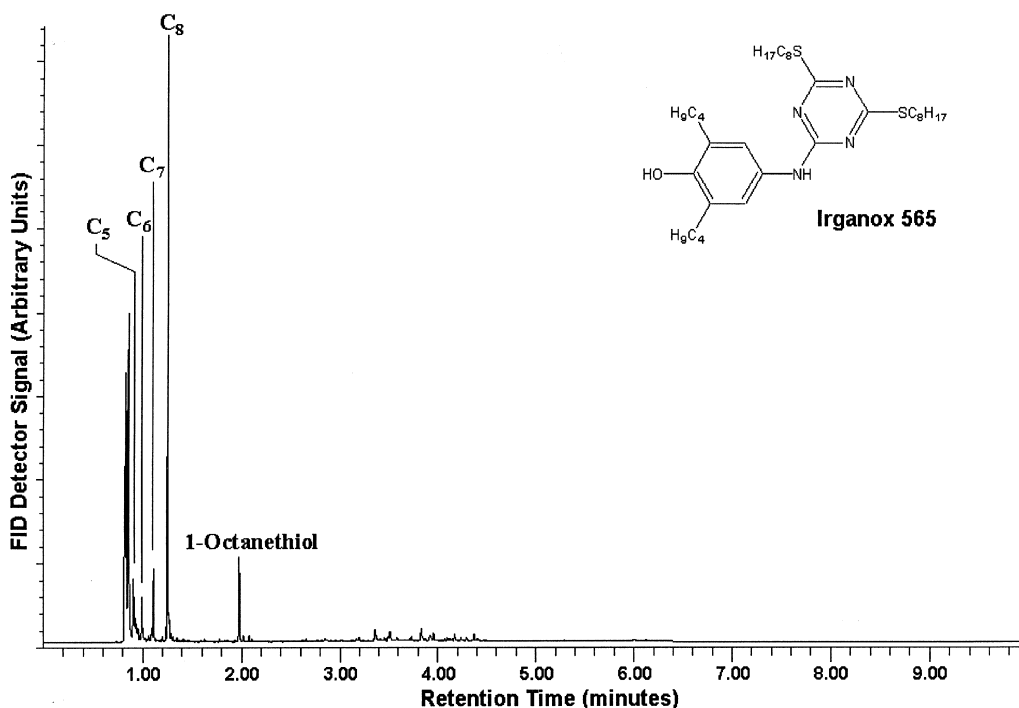


Fig. 9. The pyrogram of Irganox 565 and its structure. The chemical name is 4-[[4,6-bis(octylthio)-*s*-triazin-2-yl]amino]-2,6-di-*tert.*-butylphenol.

tional group that indicates the efficiency of pyrolysis in the octylthiol is much higher than the rest of compound. The fragments of hindered phenol unit can hardly be found in the pyrogram in this case. The positive identification of the Irganox 565 has to lie on the detection of octylthiol related of pyrolysates.

A thermoplastic resin of GE Cyclocol C 3600, which is the blend of polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS) and polymethyl methacrylate (PMMA), has been used to test of antioxidant to evaluate this Py–GC approach. The additives extract was prepared by following steps. (1) Weigh 0.5 g resin to 5 ml chloroform, shake until the resin is completely dissolved. (2) Add 10 ml methanol to the solution to precipitate out the polymer. (3) Separate the solid and solution; concentrate the solution to several drops. (4) Deposit those drops into a quartz tube for pyrolysis experiment. Fig. 10 shows the pyrogram of additives extract. Peaks labeled from A to D are monomers from the

original polymer matrix. Although the polymer has been purposely separated out from this additive extract, the monomer pyrolysates were still detected. Based on the pyrolysates identified, there are fragments from Irganox 1076 (peaks 10, 11, and C₁₁ to C₁₈), and Irgafos 168 (peaks 32–34, and peaks 35–37). In addition, both Irganox 1076 (peak 14) and Irgafos 168 (peak 40) have been found that indicates the antioxidant package used in this resin is a combination of primary (Irganox 1076) and secondary (Irgafos 168) antioxidants, used to take advantage of synergistic effects.

4. Conclusion

Antioxidants are some of the most important polymer additives used in thermoplastics. Because of the quantity used and the similarity in structure, it requires a significant amount of effort to separate and identify them. The Py–GC technique provides an

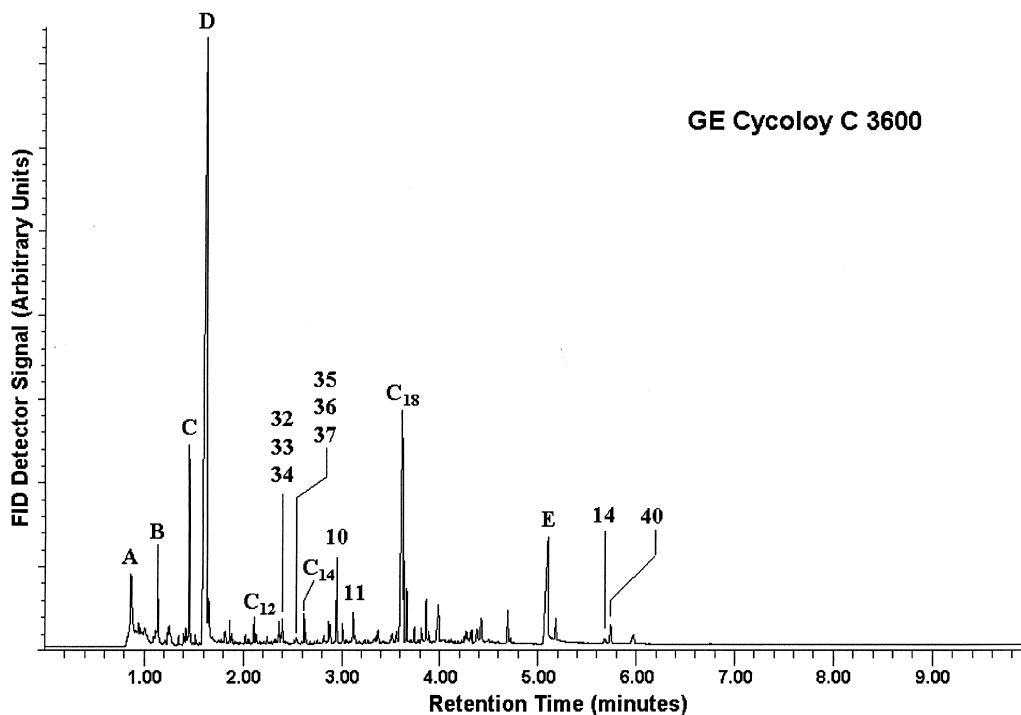


Fig. 10. The pyrogram of additive extract of GE Cyclocol C 3600 thermoplastic resin. The peaks labeled in the pyrogram have been identified and listed Tables or in Fig. 2 and Fig. 8. In addition, the other peaks are (A) butadiene, (B) methyl methacrylate, (C) styrene, (D) phenol and (E) triphenyl phosphate.

approach to minimize the sample preparation followed by an effective separation and identification in one step. The compounds investigated in this study are those commonly used antioxidants. In the GE Cycloyl C 3600 thermoplastic resin study, Py–GC was able to demonstrate that specific pyrolysates can be identified to correlate back to different antioxidants with very similar structural components. This study proves that Py–GC can be applied as another approach to analyze the antioxidants in the polymer.

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