Chapter

Pyrolysis-GC/MS, A Powerful Analytical Tool for Additives and Polymers Characterization

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Abstract

Analytical Pyrolysis technique hyphenated to GC/MS is used to obtain structural information of macromolecules. The composition and relative abundance of the pyrolysis products are characteristic for a given polymer and their determination allows the identification of materials that cannot be determined otherwise. In the present work different examples are presented in which different pyrolysis techniques are used, such as pulsed, fractional and sequential pyrolysis, working with polymer solutions, cold injection in split or narrow band mode or thermochemolysis. Specially useful is serial pyrolysis which is performed in two or more steps. Initially, volatile compounds are thermally extracted from the sample at a relatively low temperature (thermal desorption), and then the same sample is pyrolyzed at a higher temperature.

Keywords: pyrolysis-GC/MS, thermal desorption-GC/MS, polymer, additive

1. Introduction

Analytical Pyrolysis technique hyphenated to GC/MS is used to obtain structural information of macromolecules by GC/MS analysis of their thermal degradation products in the absence of oxygen [1–4]. By Py-GC/MS the polymers are converted into lower molecular weight products by the action of heat. The relative proportions of the produced products depend on the composition of the samples, the temperature and the time it is applied. The composition and relative abundance of the pyrolysis products are characteristic for a given polymer and their determination allows the identification of materials that cannot be determined otherwise. This technique can also provide quantitative analysis of polymer structure, including monomer composition, stereochemistry, tacticity, and molecular arrangements in homo and copolymers [5].

Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (RMN) and thermal analysis techniques such as thermogravimetric analysis and differential scanning calorimetry (DSC) are relevant techniques for the analysis of polymers. Py-GC/MS is a complementary technique which provides useful information that allows a deeper characterization and identification of these polymers.

Real cases often deal with the characterization of unknown samples. In these cases, it can be challenging to select appropriate instrument set-up and method
parameter starting points. However, based on the experience, there are some general considerations on how approach method development in the most efficient way.

Py-GC/MS of polymeric materials is a very powerful technique as it allows the identification of polymer components from a complex pyrolyzate mixture using a library search approach [6–21]. Besides, there are commercial pyrolysis libraries that can be a really useful help.

In more complex cases simple mass spectral identification via library (e.g. NIST, Wiley, etc.) comparison will be of limited use. A database approach is very helpful for automating the extraction of meaningful information simplifying the data evaluation task [22]. This approach consists basically of three steps: measuring reference substances to generate a database, measuring unknown or difficult samples and using the database for the identification of these samples.

Using chemometric methods can help extract useful information in very complex samples [23, 24].

Py-GC/MS has a lot of benefits [25, 26] that makes this technique a really powerful one: Pyrolysis of polymeric materials as a sample introduction technique for gas chromatography allows studying materials and compounds that are not suitable for traditional GC/MS analysis; it allows studying polymeric structures from pure systems to multi-block polymers; it requires minimal sample preparation and solvent is not required for most applications, meaning that low concentration monomers, residual solvents, additives and crosslinking agents can be identified without adding additional contaminants.

Most of the instruments allow different pyrolysis techniques [27, 28], such as stepwise pyrolysis (the sample temperature is raised stepwise, and the pyrolysis products are recorded between each step), fractional pyrolysis (A pyrolysis where the sample is pyrolyzed under different conditions in order to investigate different sample fractions), sequential pyrolysis (the same initial sample is repeatedly pyrolyzed under identical conditions: final pyrolysis temperature, temperature-rise time and total heating conditions), cold injection in split or narrow band mode (the pyrolysis products can be transferred to the GC/MS with a cold injection system) or thermochemolysis (thermally assisted hydrolysis and methylation (THM)) to improve the chromatographic analysis of polar functional groups, such as carboxylic acids.

Besides it is possible to work with polymer solutions, subsequently venting the solvent, which enables the highly precise introduction of small amounts of polymer in solution.

Another advantage of this technique is that it requires small amount of sample [25], in the range of micrograms to milligrams, typically with 300 μg of polymer a complete characterization is possible.

The technique has also some limitations [28]. Some of them are: to obtain reliable comparisons between different laboratories reproducible experimental conditions are required; inhomogeneous samples can have variable results; it does not detect most inorganic components; it is a destructive technique.

Quality control in production, product development and forensic science are some of the key areas where py-GC/MS is applicable.

In this chapter some case studies are shown as real examples from the industry to highlight the technique’s potential.

2. Practical examples

Some real examples will be presented to show the potential of this technique. The work presented in this section was carried with a pyrolyzer from Gerstel (see
Figures 1 and 2), that can pyrolyze solids and liquids in a temperature range from 350°C up to 1000°C in a very flexible and automatic way [29], and determine thermal decomposition products in the GC/MS. All spectra were obtained under electron impact (EI) conditions. Ionization voltage: +70 eV. The MS was used in the full scan mode.

### 2.1 Chemical characterization of a synthetic foam by Py-GC/MS

The application of this technique to the analysis of polyurethanes offers information about the isocyanate and the polyester or polyol used in their formulation. Three reaction mechanisms have been proposed to account for the products arising from the thermal or pyrolytic degradation of the urethane portion of a polyurethane [30, 31]. The first one is the dissociation of the urethane linkage to form an isocyanate and an alcohol, the second is the formation of a primary amine, an olefin and carbon dioxide (CO₂) via a six-membered transition state and the third is the loss of CO₂ to produce a secondary amine. The three mechanisms are shown in Figure 3.

Methylene diphenyl diisocyanate (MDI) is a diisocyanate that exists in a pure or a polymeric form. The pure one is made up of three positional isomers, shown below (Figure 4):
Figure 5 shows some possible products produced in the pyrolysis of a polyurethane made with MDI.

The foam was analyzed by py-GC/MS at a pyrolysis temperature of 600°C. By studying the pyrogram (Figure 6) the following conclusions can be obtained: the sample is a polyurethane formulated from a polyether with styreneacrylonitrile (SAN) and MDI, and although none of the three isomers of MDI monomer was detected, its diamine, 4,4'-diaminodiphenylmethane (MDA), is present and also some other degradation products, such as p-tolyl-isocianate, and a phenyldiurea. The main identified products are shown in Table 1.
Some of the products detected were produced during pyrolysis mediated between the generated radicals, including monomers in the polymer matrix, as well as acrylonitrile and styrene.

Table 1.  
*Identified products.*

| RT (min) | Compound | Match |
|----------|----------|-------|
| 2.44     | propylene | 906   |
| 2.59     | acetaldehyde | 803   |
| 2.63     | 2-butene | 683   |
| 3.00     | acetone | 870   |
| 3.35     | acrylonitrile | 877   |
| 7.34     | diisopropyl ether | 850   |
| 7.72     | 1-(1-methyletoxi)-2-propanone | 928   |
| 9.27     | styrene | 969   |
| 12.50    | p-tolyl-isocianate | 847   |
| 23.68    | palmitic acid | 886   |
| 25.62    | stearic acid | 831   |
| 25.77    | 4,4′-diaminodiphenylmethane | 963   |
| 25.97    | 1,1′-(2-methyl-1,4-phenylen)diurea (proposed compound) |  |
Py-GC/MS provides very relevant information on the monomers used in the polyurethane formulation.

2.2 Chemical characterization of a paraffin inhibitor additive

A paraffin inhibitor additive was analyzed by py-GC/MS at a pyrolysis temperature of 600°C. The pyrogram is shown in Figure 7.

![Py-GC/MS of the paraffin inhibitor additive.](image)

The following products were detected after the pyrolysis of the sample (See Tables 2–4):

| Compounds                        | Area% |
|----------------------------------|-------|
| Aromatic fraction                | 57.4  |
| Methacrylates                    | 15.3  |
| Acrylates                        | 3.2   |
| C3 and C4 olefin fraction        | 20.7  |
| Methacrylic acid                 | 0.6   |
| Olefins                          | 2.8   |

Table 2. Relative composition expressed as area percentage.

| Methacrylates fraction           | RT (min) | Area% | Match |
|----------------------------------|----------|-------|-------|
| Octadecyl Methacrylate           | 27.47    | 47    | 933   |
| Eicosanyl Methacrylate           | 28.42    | 11    | 861   |
| Docosanyl Methacrylate           | 30.24    | 43    | 847   |

Table 3. Relative composition of the methacrylate fraction expressed as area percentage.

| Acrylates fraction               | RT (min) | Area% | Match |
|----------------------------------|----------|-------|-------|
| Dodecyl Acrylate                 | 20.20    | 61    | 931   |
| Tetradecyl Acrylate              | 22.36    | 39    | 822   |

Table 4. Relative composition of the acrylate fraction expressed as area percentage.
• Aromatic cut, in the range between the boiling points of benzene and methyl naphthalenes.

• Methacrylates of C16, C18, C20 and C22 alcohols (even with their olefins, product of their thermal degradation)

• Acrylates of C12 and C14 alcohols (even with their olefins, product of their thermal degradation)

• A light C3 and C4 hydrocarbons cut (olefins).

• Traces of methacrylic acid.

2.3 Chemical characterization of lubricity improvers additives

Samples were analyzed by py-GC/MS at a pyrolysis temperature of 600°C. The pyrograms are shown in Figure 8.

The pyrolysis of the second lubricity improver additive generates a complex mixture of products mainly with saturated and monounsaturated C16 and C18 hydrocarbon chains, they are generally quite branched, and they are presented in the following families of products, always in the form of a mixture of isomers:

• Olefins.

• Alkenyl-succinic anhydrides.

![Figure 8.](image_url)

*a) Py-GC/MS of lubricity improver additive 1 and b) 2.*
• Esters of palmitic and stearic acids.

• The rest of the detected products are:
  ◦ Mix of linear mono-olefins C6 to C13.
  ◦ Palmitic and stearic acids.
  ◦ Succinic anhydride.
  ◦ 2-hydroxyethanol acrylate.
  ◦ C4 fraction (butenes)
  ◦ Ethylene glycol.
  ◦ Traces of aromatic fraction (benzene-naphthalene)

The pyrolysis of the second lubricity improver additive produces species similar to that of the previous one, with the only difference in the length of the hydrocarbon chains, which in this case are mostly C14 and C16.

2.4 Chemical characterization of viscosity index improvers additives

Four viscosity index improvers additives were analyzed by Py-GC/MS at a pyrolysis temperature of 600°C. The pyrograms are shown in Figures 9 and 10.

Figure 9.
Py-GC/MS of two of the viscosity index improvers additives.

Figure 10.
Py-GC/MS of two of the viscosity index improvers additives.
The obtained chromatograms make it possible to identify the compounds from the pyrolysis of the polymeric fraction:

- Mono-olefins
- Methacrylates
- A mixture of hydrocarbons of mineral origin.

By normalizing the response of the detected alkyl-methacrylates (Figure 11), the comparative results that are shown in Tables 5 and 6 are obtained. Traces of methacrylic acid are also detected in all four samples. Poly(methylmethacrylate) is formed by a polymerization reaction of methyl methacrylate.

![Figure 11. Poly(methyl methacrylate) formation.](image)

| RT (min) | Compound               | Additive 1 | Match | Additive 2 | Match |
|----------|------------------------|------------|-------|------------|-------|
| 5,82     | Methyl Methacrylate    | 43,40      | 907   | 51,72      | 890   |
| 10,83    | Butyl Methacrylate     | 1,51       | 925   | 0,31       | 702   |
| 20,65    | Decyl Methacrylate     | 0,30       | 821   | 0,00       |       |
| 21,81    | Dodecyl Methacrylate   | 35,67      | 951   | 29,00      | 946   |
| 22,83    | Tridecyl Methacrylate  | 0,52       | 851   | 0,00       | 838   |
| 23,86    | Tetradecyl Methacrylate| 14,67      | 894   | 15,39      | 900   |
| 24,80    | Pentadecyl Methacrylate| 0,40       | 869   | 0,09       | 806   |
| 25,73    | Hexadecyl Methacrylate | 2,97       | 905   | 3,32       | 881   |
| 27,47    | Octadecyl Methacrylate | 0,56       | 840   | 0,17       | 781   |
|          | Mineral base (on the total) | 6,90   |       | 3,37       |       |

Table 5. Relative composition expressed as area percentage.

| RT (min) | Compound               | Additive 3 | Match | Additive 4 | Match |
|----------|------------------------|------------|-------|------------|-------|
| 5,82     | Methyl Methacrylate    | 40,86      | 905   | 64,66      | 904   |
| 15,50    | 2-Ethylhexyl Methacrylate| 1,34  | 787   | 0,00       |       |
| 21,82    | Dodecyl Methacrylate   | 42,31      | 947   | 25,16      | 943   |
| 23,86    | Tetradecyl Methacrylate| 13,08      | 894   | 8,54       | 887   |
| 25,73    | Hexadecyl Methacrylate | 2,41       | 899   | 1,64       | 854   |
|          | Mineral base (on the total) | 16,77 |       | 17,88      |       |

Table 6. Relative composition expressed as area percentage.
The polymer fraction of the four samples can be described as mixtures of polymethyl-methacrylate (PMMA) with poly-alkyl-methacrylates (PAMAs) in an approximate ratio 1:1, the latter mainly with C12, C14 and C16 radicals.

All samples show signals corresponding to hydrocarbon bases of mineral origin in the boiling point range between 1-dodecene and 1-octadecene.

Obtained data are based on:
Normalization of areas of the methacrylate fraction, for the distribution of the alkyl groups.
Signal of the mineral base by contribution of areas to the total ionic current diagram.
These data are not quantitative, so they can only be interpreted in comparative terms.

2.5 Determination of maleic anhydride (MAH) in polypropylenes and ethylene-butyl acrylate (EBA) copolymers to establish the relationship between free and grafted MAH in the polymeric matrix

Two samples of homopolymer polypropylene and three EBA samples were analyzed by TD-GC/MS and Py-GC/MS. These are two base resins that have been subjected to grafting processes with MAH at theoretical contents of around 1%. The samples have been analyzed with two different methodologies:

- Thermal desorption in two stages: 100°C and 320°C for each sample. Determination of the volatiles detected in the analysis at 100°C is carried out and the residual sample is subsequently subjected to a second thermal desorption at 320°C.

- Pyrolysis: samples are subjected to 340°C for a period of time, and then, the temperature of the pyrolyzer is increased to 800°C. The products are transferred directly to the chromatographic column without being cryogenically focused, thus avoiding that various fractions of the same compound emitted at different times during the heating of the pyrolyzer coexist in the liner.

With the first methodology the chromatograms that were obtained showed peaks corresponding to the presence of MAH. However, the sum of the two obtained signals is adjusted to MAH contents two orders of magnitude lower than the MAH used in the preparation of the samples, consequently, the MAH detected in the two cases must be assigned to the free MAH. So, the MAH that was detected in the analysis at 320°C cannot be consider as grafted MAH.

The tests carried out by pyrolysis (see Figure 12) show a single MAH signal per sample, this leads to think that the grafted MAH has not been detected as such. As it is part of the polymer chain, the MAH is incorporated by the double bond of its molecule, that is, as succinic anhydride units (Figure 13), pyrolysis does not make the grafting on

![Figure 12.](image)

Py-GC/MS (pyrolysis temperature of 850°C) of one of the grafted EBA samples.
the polymer reversible, derivatives of polymeric matrix and succinic anhydride are generated, which makes it impossible to directly estimate the fraction of MAH grafted. Non-destructive spectroscopic (IR, NMR) techniques are recommended for this purpose.

2.6 Identification of deposits in filters of an Electrodeionization (EDI) unit for water purification in an industrial complex

In the filters of an EDI unit some deposits have been formed causing unit clogging. The cause of the obstruction could be a phenolic epoxy paint that had been used recently. It was thought that over time some components of said paint dissolve in water and were the deposit formation cause.

A detailed analysis of the paint and the deposit was done in order to identify if the deposits formed correspond to any of its components and which component could be the cause.

The samples were analyzed by TD-GC/MS and Py-GC/MS. Figures 14 and 15 show the thermal desorption (at a temperature of 350°C) and the subsequent pyrolysis (at a temperature of 650°C), respectively, of the paint sample.

With the analytical conditions that were tested, benzyl alcohol, phenol and phenolic derivatives were mainly detected. These compounds are compatible with a phenolic epoxy paint. See Tables 7 and 8.

2.7 Polyethylene and polypropylene artificial weathering

A method of analysis of Polyethylene, Polyethylene waxes and Polypropylene by thermal desorption and pyrolysis in series coupled to GC/MS was developed.

Optimal analysis conditions were sought for each matrix, testing different temperatures of thermal desorption and pyrolysis.

The objective is twofold. On the one hand, it is about obtaining information on the products that could be generated during a future biological and/or thermal
degradation of polymers, and on the other hand, having information on the type of polymer and additives that they might contain.

Sample 1, sample 3 and sample 5 were a virgin polyethylene, a virgin polyethyleneic wax and a virgin polypropylene sample, respectively. They were oxidized in an oven at 96°C for 28, 21 and 7 days, respectively. The corresponding oxidized samples were Samples 2, 4 and 6, respectively.

Table 7.
Identified compounds (DT-GC/MS) with area % > 1.

| RT (min) | Compound | Match | Area     | Area % |
|----------|----------|-------|----------|--------|
| 18,95    | Phenol, 4,4’-methylenebis- | 897   | 46,657,339 | 10.6   |
| 6,19     | Phenol   | 929   | 38,255,006 | 8.7    |
| 3,64     | C4 Olefin | 744   | 29,689,766 | 6.7    |
| 18,34    | Phenol, 2-[(4-hydroxyphenyl)methyl]- | 922   | 28,302,868 | 6.4    |
| 3,62     | Propane  | 677   | 26,265,730 | 6.0    |
| 7,13     | Methylphenol | 920   | 24,482,943 | 5.6    |
| 7,39     | Methylphenol | 917   | 18,073,779 | 4.1    |
| 3,97     | Benzene  | 867   | 17,241,399 | 3.9    |
| 4,39     | Toluene  | 876   | 13,477,989 | 3.1    |
| 3,74     | Cyclopentadiene | 710   | 11,580,548 | 2.6    |
| 19,58    | 4,4’-Ethylidenephophenol | 731   | 7,498,180  | 1.7    |
| 4,27     | Dimethylciclopentene | 801   | 6,978,780  | 1.6    |
| 19,89    | 9,10-Anthracenedione, 1,4,4a,9a-tetrahydro- | 704   | 6,006,814  | 1.4    |

Table 8.
Identified compounds (Py-GC/MS) with area % > 1.

Figure 15.
Py-GC/MS of the paint sample (650°C).
Figure 16.
a) DT- and b) Py-GC/MS of sample 1.

Figure 17.
a) DT- and b) Py-GC/MS of sample 2.
Figure 18.
a) DT- and b) Py-GC/MS of sample 3.

Figure 19.
a) DT- and b) Py-GC/MS of sample 4.
Figure 20.  
a) DT- and b) Py-GC/MS of sample 5.

Figure 21.  
a) DT- and b) Py-GC/MS of sample 6.
Figure 22. Fragmentogram m/z 60 DT-GC/MS of the polyolefin samples a) 1 and b) 2.

Figure 23. Fragmentogram m/z 60 DT-GC/MS of the polyolefin samples a) 3 and b) 4.
The six samples were analyzed by TD-GC/MS and the residual of each sample is subjected to Py-GC/MS. The following figures show the chromatograms that were obtained for the polyolefin samples. The Polyethylenic wax and Polyethylene pyrograms consists of serial triplets, corresponding to α, ω-alkadienes, α-alkenes and n-alkanes, respectively, in the order of increasing n + 1 carbon number in the molecule. See Figures 16b, 17b, 18b and 19b. Identification of compounds was carried out by comparison of mass spectra with data in the NIST mass spectral library.

The pyrograms of the Polypropylene samples show branched alkenes (C4 to C13) as major components. Isobutene, 2-methyl-2-butene, 3-methyl-1-pentene, dimethylpentadienes, 2,4-dimethyl-1-heptene are the most abundant branched alkenes. See Figures 20b and 21b.

In the m/z 60 fragmentograms of the oxidized Polyethylene and Polyethylenic wax samples (See Figures 22b and 23b) carboxylic acids are detected. In the m/z 60 fragmentogram of the oxidized Polypropylene no carboxylic acids are detected (See Figure 24b). In the TIC of this sample acetone is detected. However, in the pyrograms, no carboxylic acids, aldehydes or ketones are detected.

3. Conclusions

This chapter is intended for the use of both researchers and chemists who use GC/MS to analyze materials, and who need to add pyrolysis techniques to their analysis tools. Py-GC/MS is a practical, cost-effective, reliable, and flexible alternative for increasingly complex sample analyses, and can be used to analyze different
kind of samples for a diversity of fields including industrial research, microbiology, forensic science, and environmental analysis.

The potential of Py-GC/MS was highlighted through different case studies, ranging from additives chemical characterization to weathered polyolefins samples.

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**Conflict of interest**

The author declares no conflict of interest.

**Notes/thanks/other declarations**

At Repsol Technology Lab we offer equipment and knowledge to apply Py-GC/MS to polymers and additives adapted to customer needs.

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