

The Use of Pyrolysis-GC/MS and Newly Developed Libraries to assist in Characterizing Complex Polymeric Systems

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ABSTRACT

There are several analytical techniques that can be used to analyze for individual components in a polymeric sample including FTIR, solvent extraction-GCMS, TGA-MS, HPLC, among others. However, these techniques do not normally lend themselves to analyze for the complete polymeric system, which includes volatile and semi-volatile compounds and the actual polymer. But using a pyrolyzer as a "thermal extracting introduction system" in combination with any industry standard GCMS provides a simple and direct means of analyzing not only the additives, but also the polymer itself. By careful selection of the sampling temperature, volatile and semi-volatile compounds may be liberated from the polymer matrix for analysis without the use of solvents or complex sample preparation. The remaining sample may then be pyrolyzed to identify the type and even structure of the polymer used in its fabrication. A typical series of analyses includes a low temperature assessment to identify volatile additives, contaminants and residuals, such as solvents and retained monomer. An intermediate temperature is used to investigate semi-volatiles like antioxidants, plasticizers and lubricants. Finally, at pyrolysis temperatures, the polymer itself may be identified and studied.

In addition, there are commercially available libraries developed to help identify different categories of additives and polymers using the search programs from the GCMS system. This poster will look at several examples of plastics and rubbers to identify the additives, residual monomers and the polymers using specially developed libraries and standard GCMS search software.

EXPERIMENTAL

A CDS Analytical Model 5200 Pyroprobe was interfaced to an Agilent 7890 GC with a 5973 MS detector to analyze these samples. Each analysis used approximately 100 micrograms of sample and was heated inside a quartz sample tube. The quartz tube with the sample was placed in a platinum filament and pyrolyzed at up to 3 different temperatures, with a GC run on each step. The resulting volatiles were transferred via a heated transfer line to the gas chromatograph for analysis. The GC was equipped with a 30 meter 5% phenyl column, which was held at an initial temperature of 40°C for 2 minutes, then ramped at 8°C per minute to a final temperature of 300°C, which was held for 5 minutes. The detector was set to scan from 25 to 550 amu.

RESULTS/DISCUSSION

Depending on the requirements of the manufacturer, plastic packaging may employ several polymers, in layers or blends. In addition, food grade additives may be added to the packaging to improve flexibility, to provide protection from oxygen or light, prevent flavor scalping, among others. The pyrogram from a clear plastic package in figure 1 looks much like polyethylene (PE), but there are additional peaks, one of which is benzoic acid. Placing the product pyrogram between PE and polyethylene-terephthalate (PET) as shown in figure 2, shows that the peaks are coming from a mixture of these two polymers. The largest peaks in PET are labeled 1-4, and are also present in the sample. Four peaks from PE are labeled 5-8 but it is clear that all peaks from PE are in the sample as well.

A single step analysis of a sample, such as the one in Figure 1, contains all the peaks made by pyrolyzing the polymer, and may contain small peaks for volatile and semi-volatile compounds as well. The peaks for residual monomers, additives and contaminants may be difficult to see among all the larger peaks made from pyrolysis. By heating the sample material to temperatures hot enough to volatilize these components, but not so hot as to pyrolyze the polymer matrix, the analytes can be separated into thermal families of compounds for easier analysis.

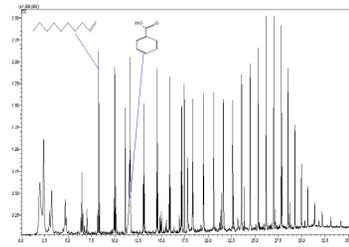


Figure 1. Pyrogram of clear plastic food packaging

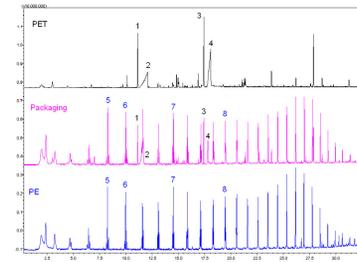


Figure 2. Pyrogram of clear packaging with PET above and PE below

If the plastic packaging from figure 1 was first heated to 200°C, small peaks for sorbic and benzoic acid are produced, as well as a small peak for a phthalate plasticizer, as shown in Figure 3. At 400° there is more of the plasticizer, a series of paraffin's, and a diisocyanate. Diisocyanates are the primary pyrolysis products of polyurethanes, which degrade at a much lower temperature than the polymer matrix of the packaging. The paraffin's could be residuals from lubricants, or from the polyethylene in the packaging polymer. At 700°C, the polymer itself is pyrolyzed, producing a pyrogram much like the one in Figure 1. Triplet peaks for normal hydrocarbons are generated from polyethylene and aromatics from the PET.

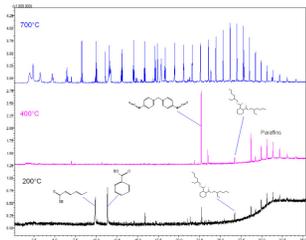


Figure 3. Tri-step analysis of packet

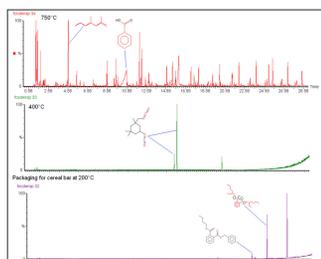


Figure 4. Tri-step analysis of packaging for cereal bar

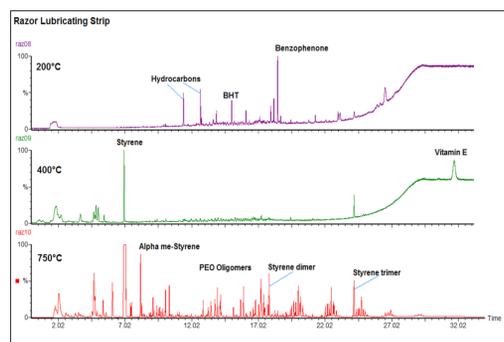


Figure 5



Razor Lubrication Strip from Figure 5

In figure 5, we pyrolyzed a rubber lubricating strip from a disposable razor. We used three temperatures starting at 200C then 400C and finished at 750C. The compounds seen at 200C include two additives, the antioxidant Butylated Hydroxy Toluene (BHT) and a UV light stabilizer, Benzophenone. Also included are some hydrocarbons that act as the lubricant for the strip. At 400C we see what is probably a residual monomer, styrene, and the addition of vitamin E oil. The razor packaging advertises that it is good for the skin so they are true to their word. On our last run at 750C, we now are looking at the remaining polymer fragments. We have styrene monomer, dimer and trimer from the polystyrene and a series of oligomers made from Polyethylene Oxide.

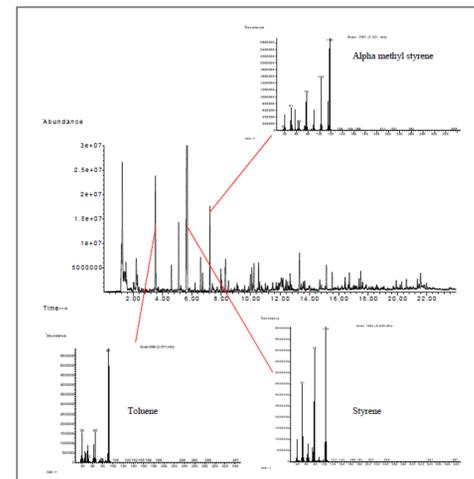


Figure 6

Figure 6 shows a rubber sample that was pyrolyzed at 750C. If the mouse button is held down and the cursor dragged across the entire pyrogram, an average spectrum is produced for the whole run, with masses from all the peaks in the pyrogram. This spectrum is then searched against the pyrolysis library as seen in figure 7. The library indicates that it is a copolymer of styrene/butadiene.

For new users of pyrolysis or when searching samples for unknown compounds, it would be helpful to use a customized data base to identify the polymers and additives. In many cases, the additives are in very small quantities and are not easily identified, even with a NIST library. The next two examples use a polymer and additive library to search for polymer identification as well as additives by category. The polymer library was built by running standards of over 400 polymers and averaging the spectra from each of the runs. A file was added into the library for each of these polymers. After a sample is run, the library can then be searched for a match using the GC/MS software to search the polymer library.

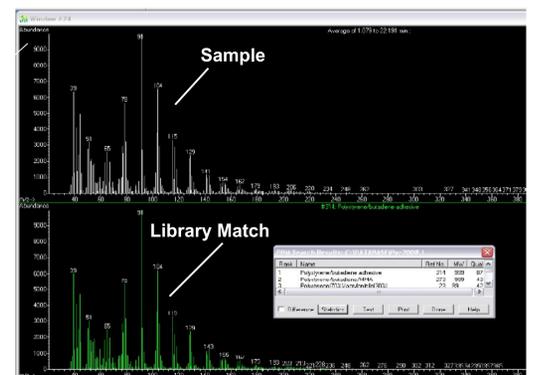


Figure 7

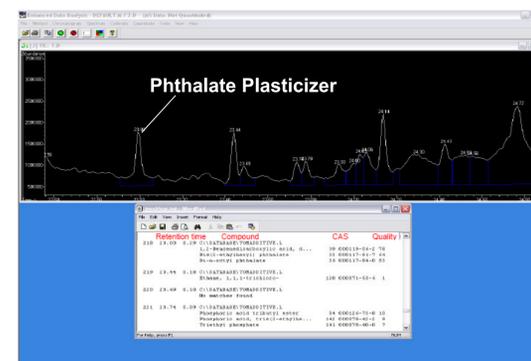


Figure 8

If you now desire to look for any additives, you could search the additive database by category, such as plasticizers, antioxidants, light stabilizers, flame retardants etc. In this case, we searched for plasticizers using Agilent's Chemstation software and searched our library for a match. A phthalate plasticizer was found at 23 minutes, as shown in figure 8.

CONCLUSION

Pyrolysis-GC/MS can take on the role of several analytical techniques allowing the user to determine the total make up of a polymeric sample, including volatiles, semi-volatiles and the polymers themselves. And as an added benefit, running samples at a minimum of 3 temperatures makes the data easier to interpret since there are fewer peaks in each run. This will also help confirm that all the peaks in the final run are fragments from pyrolysis of the polymers, not from additives. Often, you may see a pyrolysis product (like Benzoic acid) also used as an additive. So, running the samples at pre-pyrolysis temperatures (below 400C) first, confirms if it is an additive or polymer fragment.

With the implementation of specially designed polymer libraries, the identification of polymers from the fragments as well as the search for individual additives can be achieved by pyrolysis novices. And, it is possible to use the libraries with search programs that the user may already be familiar with, such as Agilent's Chemstation and AMDIS, eliminating a learning curve with a new software package.