GAS CHROMATOGRAPHY/MASS SPECTROSCOPY FOR PLASTICS FAILURE ANALYSIS

Myer Ezrin and Gary Lavigne
Institute of Materials Science
University of Connecticut
Storrs, CT 06269-3136

1.0 Abstract

Gas Chromatography/mass spectroscopy is particularly useful as an analytical method for plastics failure analysis in cases where detection of an unknown contaminant or other compositional factor may be the cause or a contributor to failure. It takes advantage of the fact that GC is a method of separating compounds in a mixture, permitting their identification and possibly quantification. MS is not only a very sensitive detector but also gives mass spectra of GC peaks, permitting their identification in many cases.

In thermal desorption GC/MS compounds are transferred from the sample to the GC with heat. Completely nonvolatile materials are not detected. Using desorption temperatures up to 300-350°C, many components of plastics can be analyzed. In pyrolysis GC/MS the sample is decomposed at temperatures up to 900°C; GC/MS analyzes the pyrolyzate. Examples are given of causes of plastics failures that have been determined by GC/MS.

2.0 Introduction and Description of GC/MS Methods [1,2]

Failure analysis often requires compositional analysis, e.g., to identify a contaminant. We include under "plastics failure analysis" cases in which a company is accused of being the source of a product that failed in service. In fact, another company may be the source of the failed product. It may be possible to determine the source by analyzing for a distinctive material that is unique to a company's product.

Infrared spectroscopy (IR) is a useful method in plastics analysis. In many cases, however, it is not sensitive enough to detect trace materials. The spectrum may be of a complex mixture, making the spectrum of little value. Chromatography is a separation method from which compounds of a complex mixture can be identified and possibly quantified. In gas chromatography, for a material to be detected, it has to be sufficiently volatile to pass through a GC column at a temperature that may be as high as 300-400°C under helium gas flow.

Solvent extraction is a common way of separating extractable compounds from a mixture, followed by injection of the solution into the GC. In thermal desorption GC, also called thermal extraction GC, no solvent is used – only heat at a controlled temperature such as 2 minutes at 200-300°C. Use of heat alone without solvent provides a major increase in detectability.

The description of the thermal desorption device used at the University of Connecticut can be accessed on the internet at www.ims.uconn.edu/~lavigne/gcmslab.html. Heating is isothermal, not ramped as in some commercial devices. Samples are placed upside down in a small glass or quartz tube and held in place with quartz wool. The tube is transferred into the injection port of the GC, which is the heat source for thermal desorption. The tube in the injection port is in direct contact with the head of the GC column, so that helium flow carries the volatiles directly onto the column. The absence of a transfer line is a key feature and advantage of the UConn device. The tube is removed with gas pressure at the end of the desired desorption time, such as 2 minutes. The tube can subsequently be reinjected for additional heating at the same or higher temperature as before. See also section 3.0 below.

GC peaks may be identified from their retention times, i.e., the time from injection to elution. Comparison with known compounds may provide a basis for identification of peaks, if the suspected known is available. A chromatogram may have about 50 or more peaks with little basis for knowing their identities. Thus, comparison of retention times with knowns is often not a practical method. Mass spectroscopy (MS) not only provides a measure of the quantity of each compound by peak area, it also gives a mass spectrum that often identifies the peak. Reference mass spectra are available with approximately 150,000 spectra. Spectral search by computer provides a match and spectra of knowns from the reference file to aid the analyst in identification of an unknown. For a particular compound, sensitivity can be enhanced by single ion monitoring or selected ion data collection, in which one or more dominant mass fragments are used instead of a complete mass spectrum. Mass spectroscopy also provides molecular weight of a compound, which may also be useful in identification.

Many plastics additives are sufficiently volatile to be analyzable by GC/MS, including antioxidants, stabilizers, plasticizers, mold release agents, lubricants, organic flame retardants, etc. If the concentration of an additive is incorrect, it may contribute to failure. An example is insufficient or depleted antioxidant or stabilizer.

For qualitative identification, a material does not have to be completely volatile at the temperature used, as long as the GC peak size is great enough to be detected by the mass spectrometer. For quantitative analysis, it is desirable for the compound to be sufficiently volatile so that peak area provides a measure of concentration.

Pyrolysis GC/MS is similar to thermal desorption using temperatures up to 900°C. What is analyzed are the pyrolysis products. Examples are given of both thermal desorption and pyrolysis GC/MS compositional analyses and failure analyses.

3.0 Description of the Devices

Thermal Desorption. Figure 1 is a diagram of the portion of the device that is heated in the GC injection port [3]. It shows the tube with sample being domed over the beginning of the GC column so that volatiles are transferred directly and dynamically onto the column with helium gas flow. Figure 2 is a photograph of the device. Further detail is available on the internet web site referred to above.

Another method of collecting and transferring volatiles into the GC column is to use a separate collection device in which volatiles are adsorbed on a tube containing Tenax adsorbent. A larger sample, for example, can be heated at moderate temperature such as 60-70°C for several hours. The tube with the Tenax adsorbent is in the closed container with the heated sample. Following heating and collection onto Tenax, the tube is placed in the thermal desorption device for analysis in the same manner as samples heated directly therein.

Pyrolysis. Figure 3 is a photograph of the device [4]. It uses a commercial furnace capable of up to 900-1000°C isothermally. The ability to remove sample tubes at will means that the furnace does not become clogged with samples.

Also, the same sample in the pyrolysis device can be desorbed thermally at a temperature below pyrolysis temperature, thus giving analysis of volatiles present as such. Subsequently, by raising temperature to the pyrolysis range (500-900°C) the same sample, with volatiles removed, can be analyzed by pyrolysis.

4.0 Examples of Use of GC/MS for Failure Analysis

4.1 Confirmation of source of failed product. Plastics products often are not identified as to the company that sold the product. Failures may occur years into the service history of a product. The customer may assume that the failed product was made by a particular vendor, while it could just as well have been made by another company. The accused company may want to confirm that the failed product was in fact made by them. That may be possible if there are distinguishable compositional factors between their product and the failed one.

4.1.1 Polycarbonate of different sources. It has been possible to distinguish polycarbonate from different resin suppliers by differences detected by TD/GC/MS (thermal desorption). That in turn helps to identify the source of the molded part. The differences are minor but reproducible compounds associated with one resin source and not the other.

4.1.2 Polymer used in an adhesive system. A product that was only a few percent of a polymer in an adhesive in which most of the adhesive is inorganic in nature may come back from the field as having been made by a certain adhesive manufacturer. The adhesive contains about 2% of a styrene-butadiene copolymer. Pyrolysis GC/MS readily identifies styrene and butadiene, which means that the failed adhesive may or may not have originated with the accused company [5].

4.2 Competitive analysis.

4.2.1 Identification of a crosslinking agent (Fig. 4). Peroxide crosslinking agents can be identified by their decomposition products. For example, dicumyl peroxide gives acetophenone, alphamethylstyrene and alphacumylalcohol. Ditertiarybutyl peroxide decomposes to acetone and tertiarybutyl alcohol. The presence of decomposition products provides a good basis for identification of a peroxide.

4.2.2 Identification of a component conferring unusually good adhesion (Fig. 5). In a competitive product in which adhesion of inorganic particles to a substrate is involved, the competitive product had superior performance related to adhesion of the particles to the substrate. TD/GC/MS detected triphenylphosphine and nitromethane. The phosphine is a polar compound that promotes adhesion of a polar to a nonpolar material. Nitromethane is the solvent used to apply the phosphine to the substrate to impart improved adhesion [6].

4.3 Identification of contaminants causing failure.

4.3.1 Thermally bonded package adhesion problem (Fig. 6). Silicone oil was detected in packages that were only partially bonded by the usual thermal bonding process. The silicone oil was traced to its source using TD/GC/MS. The particular composition of the oil was important in assigning the problem to the correctly identified oil since there was more than one possible silicone oil.

4.3.2 Blistered neoprene jacket on a cable lying in a field [7]. Two inch diameter neoprene jacket of a cable in service bringing power and signal information to and from a radar station was found to be highly blistered. The cable manufacturer was accused of having made a defective product. The cause of blistering was found by TD/GC/MS to be agricultural chemicals. The field was an agricultural field that was farmed. The blisters were due to agricultural chemicals sprayed on the crop, which also contacted the neoprene jacket. Non-blistered areas of the jacket did not have the agricultural chemicals, five of which were detected. Since the jacket requirements did not include resistance to agricultural chemicals, the problem was not a failure of the neoprene but the exposure of the neoprene to improper service conditions. Failure was caused by a contaminant but it was not the fault of the cable manufacturer.

4.3.3 Polymer instability due to a contaminant. Instability of a polymer, in which a volatile organic compound was generated causing product quality and safety problems, was traced to a compound that was not supposed to be present. Knowing what the foreign contaminant was permitted the determination of the source in the several possible sources comprising the polymer formulation.

4.3.4 Adhesion problem of silicone adhesive to polypropylene (Fig. 7). Silicone adhesive used to bond phenolic resin to polypropylene was unsatisfactory in a plant in which the parts to be bonded were stored openly for long periods before assembly. The surface of parts to be bonded was shown by TD/GC/MS to contain a substantial amount of hydrocarbons. They had been deposited from exhaust fumes of vehicles in the plant. Parts with surfaces free of the contaminant bonded well. The lesson was to protect surfaces to be bonded from exposure to air that contaminates the surface resulting in unsatisfactory adhesion [8].

4.3.5 Adhesion problem due to inorganic stearate salt (Fig. 8). Adhesion of an electrical power distribution cable to the conductor was less than it needed to be. TD/GC/MS detected the free fatty acids associated with stearate salts with calcium or zinc. Such material was not supposed to be present because it would lower adhesion. TD/GC/MS does not detect the stearate salt directly due to its low volatility. But the corresponding fatty acids, hexa- and octadecanoic acid were detected and constitute a practical indicator of the stearate salt.

4.4 Overcoming a problem in product development.

4.4.1 Eliminating the cause of unacceptable evolution of volatile compounds from a polymer foam. Polyurethane foam insulation used in computers and other systems has to meet strict requirements of low evolution of volatiles so that they do not contaminate electronic circuits. This is analogous to the problem of volatilization of plasticizers from PVC used in automobiles, causing fogging of the interior of windows and of mirrors. By identifying the evolved compounds from the polyurethane foam, the formulation could be adjusted to minimize their presence. In this way acceptable foam was developed that met the low volatiles and low fogging requirement. In this work the volatiles to be analyzed were collected using a Tenax adsorbent in a tube subsequently analyzed by TD/GC/MS in the usual way. The method of collection of volatiles for analysis is described above in 3.0 Thermal Desorption.

4.5 Other types of failure.

4.5.1 Absence or presence of a second component needed to obtain good adhesion. Some adhesives are two part systems that provide good bonding only if both parts are present in the correct ratio. In some failure cases, analysis determined if one of the necessary ingredients had been omitted.

4.5.2 Cause of explosion of polyethylene container of waste solvent. A polyethylene five gallon container of laboratory waste solvent exploded, shattering the PE and sending solvent all over the laboratory. No one was present and no significant damage was done. A recovered piece of the PE was analyzed by TD/GC/MS in the hope of determining the cause of the explosion. Mono and disubstituted nitrotoluenes were detected and there was an indication of a trace of trinitrotoluene (TNT). The same solvent can had been used by more than one person. Toluene was one of the waste liquids and nitric acid another. Slowly over several weeks the two reacted, with formation of the highly explosive TNT. Even though only a trace of TNT was detected, dinitrotoluenes were detected readily. Chemical logic dictates that some trinitrotoluene may also form. When it built up to a certain level, the liquid mixture became explosive. With the aid of TD/GC/MS the cause of the explosion was determined [9].

4.5.3 Solidification of a grease causing a servo motor to fail. A small servo motor used for such things as controlling the air/gasoline mixture in an automobile employs a grease on a metal screw so that the screw can move freely back and forth. Failure occurred when the grease solidified. The grease contained a polyolester as part of the formulation, as well as triphenylphosphate (TPP) liquid plasticizer. TD/GC/MS showed the presence in the failed grease of three carboxylic acids, such as heptanoic acid, not seen in unused good grease. The organic acids had been hydrolyzed off the polyolester. Apparently the TPP hydrolyzed, forming phosphoric acid, a strong inorganic acid. This in turn caused hydrolysis of the organic acids off the polyolester. The GC peak of TPP was greatly reduced. Solidification may have been due to attack of the phosphoric acid on the metal rod, which was confirmed by TGA (thermogravimetric analysis). Carboxylic acids by GC from polyolester were also indicated by IR spectroscopy. The recommendation was made, based on the analysis, that organic phosphate esters not be used in the grease. A suggestion of using tricresyphosphate was rejected because it would act similarly to triphenylphosphate [10].

4.5.4 Electrical cable failure. A cable consisting of plasticized PVC insulation and jacket developed unacceptably low insulation resistance. TD/GC/MS showed that plasticizer and other materials had migrated from the jacket into the insulation causing insulation resistance to fall to an unacceptable value. By comparing to a new cable in which there had not been migration from jacket to insulation, it was clear that the failed cables with low insulation resistance had experienced migration from the jacket [11].

5.0 Conclusions

Thermal desorption and pyrolysis gas chromatography/mass spectroscopy (GC/MS) are very sensitive, useful and versatile methods of analysis of plastics materials and products. Using heat to desorb or "extract" volatile materials from a sample gives much greater sensitivity than injection of solvent-extracted compounds. Some of the types of applications to various failure situations illustrated are as follows:

1. Confirmation of source of failed product.
2. Competitive analysis.
3. Identification of contaminants causing failure.
4. Overcoming a problem in product development.
5. Other types of failure.

6.0 References

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9. Reference 1, figure 17.
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Key Words - plastics failure analysis, thermal desorption and pyrolysis gas chromatography/mass spectroscopy.

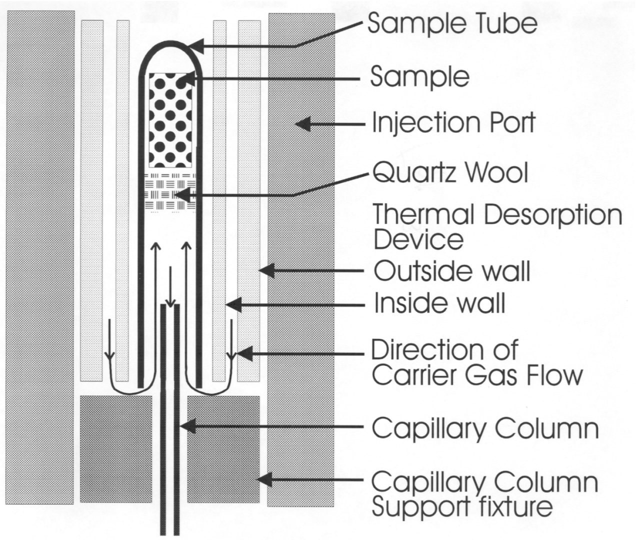

Figure 1. Position of inverted sample tube in GC injection port during thermal desorption of volatiles directly onto GC column.

Figure 2. University of Connecticut thermal desorption device for GC/MS.

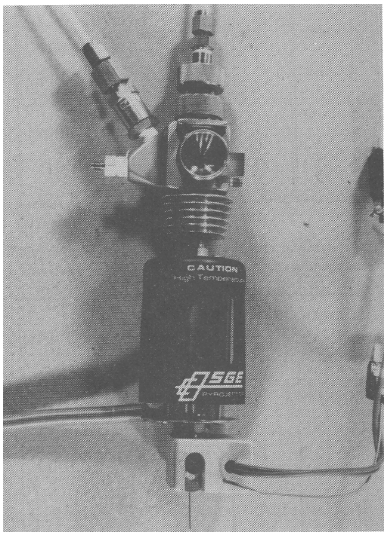

Figure 3. Pyrolysis GC/MS device.

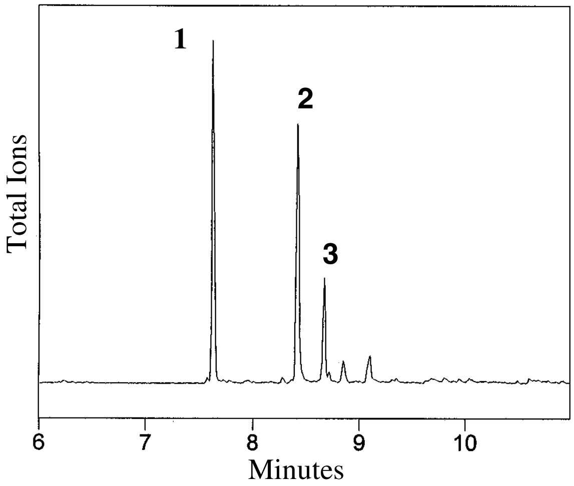

Figure 4. GC/MS themal desorption chromatogram of by-products of decomposition of dicumyl peroxide crosslinking agent; peak 1 – alphamethylstyrene, 2 – acetophenone, 3 – alphacumylalcohol.

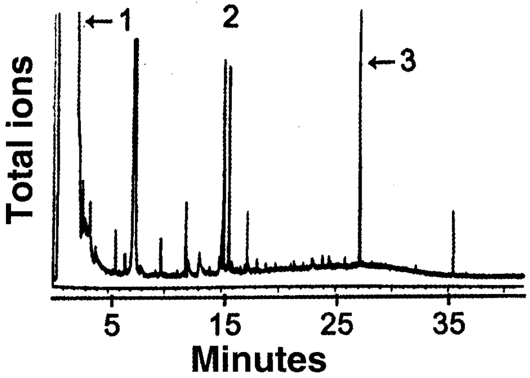

Figure 5. TD/GC/MS of coating on cloth at 150°C TD temperature; peak 1 – nitromethane, 1 – urea formaldehyde oligomers, 3 – triphenylphosphine.

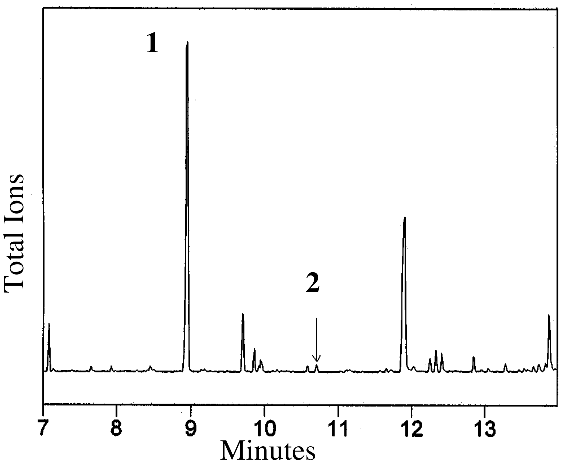

Figure 6. GC/MS thermal desorption chromatogram of silicone oil causing poor adhesion of thermally bonded package; peak 1 – octamethylcyclotetrasiloxane, 2 - decamethylcyclopentasiloxane.

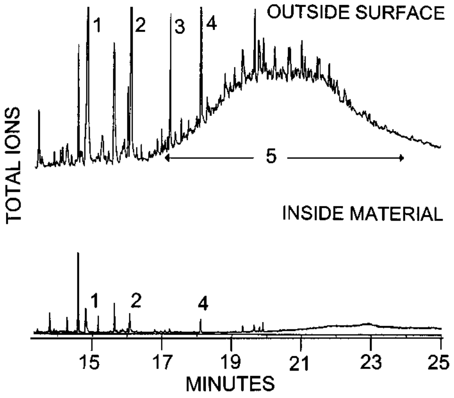

Figure 7. TD/GC/MS chromatogram of outside surface and material below the surface of phenolic part that could not be bonded well to silicone RTV adhesive; peak 1 – hexadecanoic acid, 2 – octadecanoic acid, 3 – octadecanamide, 4 – dioctylphthalate, 5 – hydrocarbons.

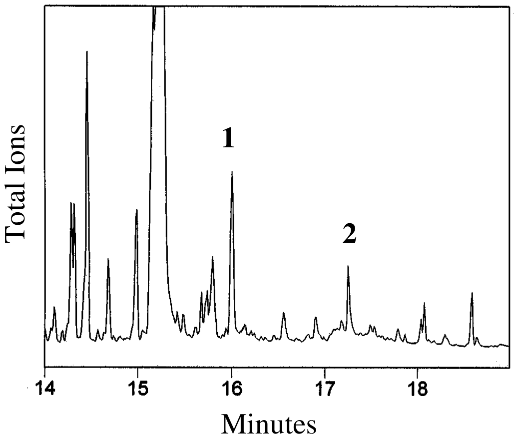

Figure 8. GC/MS thermal desorption chromatogram of fatty acids indicative of stearate salt; peak 1 – hexadecanoic acid, 2 – octadecanoic acid.