Gas Chromatography in Coatings Analysis

Francis V. Acholla—Rohm and Haas Company*

Gas chromatography (GC) is an established standard analytical tool for the analysis of coatings and related materials. Many volatile and semivolatile compounds such as residual monomers, solvents, and plasticizers, and low molecular weight additives such as mildewicides and antifoaming agents can easily be analyzed by GC. Headspace-gas chromatography/mass spectrometry (HS/GC/MS) is used for routine analysis of odor problems and for analyzing relations in situations where solvent extraction and/or simple dilution are not appropriate. Less volatile compounds, such as polymers, resins, and waxes can be analyzed by pyrolysis-GC/MS and/or derivative pyrolysis-GC/MS, such as methylation with acetyltrimethylammonium hydroxide (TMAH).

INTRODUCTION

Gas chromatography (GC) continues to play a vital role in the analysis of coatings and related materials. This article focuses primarily on those areas where new insights have emerged in the literature and in our laboratories in the last several years. The reader is encouraged to review references 1-4. Gas chromatoigaphy involves a sample being vaporized and injected onto the head of the chromatographic column. A schematic diagram of the basic components in a GC system is shown in Figure 1. The sample is transported through the column by the flow of inert, gaseous mobile phase (Ar, He, CO₂, and N₂). The choice of a carrier gas normally depends on the type of detector used. The column itself contains a liquid stationary phase, which is adsorbed onto the surface of an inert solid.

Column Packing Material

The column packing material must be capable of withstanding high temperatures (up to 350°C) and moderate pressures (up to 5 atm), and should be inert and available in different particle sizes. Other important physical parameters include particle size (smaller particle sizes provide more plates), porosity and surface area (a larger surface area which is determined by porosity will require more liquid phase to achieve a complete coating), and the packing density. Some examples of solid packing materials include Chromosorb P, which is sourced from firebrick, and Chromosorb W, which is sourced from Celite Filter Aid. Each of these packing materials may be treated with a slurry of reagents such as dichloromethane (DDMCS) to cover the active silanol functionality on the surface, or may be treated with acid or base to remove active metal contamination. Some examples of commonly used columns are described in Table 1.

Table 1—Commonly Used Columns

<table>
<thead>
<tr>
<th>Stationary Phase</th>
<th>Temperature Range</th>
<th>Applications</th>
</tr>
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<tbody>
<tr>
<td>100% Methyl polysiloxane</td>
<td>-60°C to 350°C</td>
<td>General purposes, k.p., hydrocarbons, aromatics, solvents, waxes, phenols, etc.</td>
</tr>
<tr>
<td>Polystyrene glycol</td>
<td>60°C to 200°C</td>
<td>Amines, acids, alcohols</td>
</tr>
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Figure 1—Schematic diagram of the basic components in a GC system.

Detectors Used in GC

Thermal conductivity detectors (TCD) and flame-ionization detectors (FID) are excellent detectors for routine types of analysis, for example, in Quality Control (QC), because they provide retention times which are very reproducible and are compound specific (retention times), whereas the analyses are done under the same GC conditions. The only drawback of these detectors is that they are not very specific. GC has very low detection limits, which is advantageous for quantitative analysis of monomers. Mass spectrometers (MS) are the detectors of choice when one is interested in detailed information for unknown analytes which cannot be identified accurately by retention times alone. The compounds can be identified by their retention times and/or the relative abundances of various charged fragments, as shown in Figure 3.

Pyrolysis-GC/MS

Pyrolysis-GC/MS remains the major area of GC application in coatings. Its strength is its ability to analyze nonvolatile organic samples, such as resins and polymers. Here, the GC is fitted with a pyrolysis unit, which is interfaced to a GC/MS system (Figure 4). Such an arrangement provides valuable information on a coating, ranging

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INTRODUCTION

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Detectors Used in GC

Thermal conductivity detectors (TCD) and flame-ionization detectors (FID) are excellent detectors for routine analysis of analytes. Examples of these detectors are shown in Figure 1. Where the analyses are done under the same GC conditions, the only drawback of these detectors is that they are not very specific. GC has very low detection limits, which is advantageous for quantitative analysis of monomers. Mass spectrometers (MS) are the detectors of choice when one is interested in detailed information for unknown analytes which cannot be identified accurately by retention times alone. The compounds can be identified by their retention times and/or the relative abundances of various charged fragments, as shown in Figure 3.

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<td>Polyethylene glycol</td>
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<td>-60°C to 350°C</td>
<td>Alcohols, acetates, phenols, drugs, sugars, pesticides, and herbicides</td>
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PROLYSIS-GC/MS

Pyrolysis-GC/MS remains the major area of GC application in coatings. Its strength is its ability to analyze nonvolatile organic samples, such as resins and polymers. Here, the GC is fitted with a pyrolysis unit, which is interfaced to a GC/MS system (Figure 4). Such an arrangement provides valuable information on a coating, ranging from simple structure elucidation to the presence of specific functional groups.
from solvent, plastizizers, and other additives to the determination of the polymer composition. For this method to work, the polymer must be unzipped by fast heating to temperatures greater than 400°C in an inert atmosphere. This procedure reduces the high molecular weight polymer to fragments amenable to GC analysis. Normally, the low molecular weight fragments are characteristic of the starting polymer. For example, acrylics generate large amounts of the original monomers. Typically, wet or dry samples can be analyzed either by ribbon or coil probes. The material is pyrolyzed instantly at 700–800°C for 10–20 sec. Normal pyrolysis runs are between 30–40 min. However, with high-speed GC systems, analysis time can be as short as 60–120 sec. Short analysis times are achieved with short narrow columns or high flow rates, high temperature oven ramps, and high speed detectors for high-speed separations.

Alternatively, the reduction of higher molecular weight condensation polymers to low molecular weight fractions amenable to GC analysis can be achieved via chemical degradation reactions. The low molecular weight species generated in this fashion are normally related to the starting polymer. Normally, the pyrograms are complex but can serve a variety of purposes, ranging from additives identification to providing compositional fingerprints, which can be matched to controls. Good understanding of the thermal degradation/pyrolysis mechanism is very important for proper interpretation of the results. There are three degradation paths depending on the polymer type: (1) unzipping; (2) random chain fragmentation; and (3) non-chain scission.

The peaks labeled "fingerprint fragments" in Figure 5 are also very important in polymer analysis. They can be used in product quality control analyses. Numerous practical examples of typical pyrolysis-GC and derivative pyrolysis-GC of polymers have been published by Levy and Wampler, and Washall and Wampler.

**HEADSPACE-GC**

Typically, a sample of interest is heated in a sealed container at a given temperature and time (for example, 150°C for 30 min). Then a sample of the volatiles in the sealed container (gases) is introduced into a GC system with the carrier gas. Commercially assembled systems of this kind are called Headspace analyzers.

**Representative GC Application Areas**

**RESIDUAL MONOMERS:** The residual monomer level in commercial latexes typically do not exceed 500 ppm and in many cases is below 100 ppm. Headspace GC or straight GC is an excellent method for determining the types and levels of residual monomers. In a typical GC analysis, between 5–10% of an emulsion is prepared and centrifuged to extract the residual monomers and the supernatant is injected into the GC. The detection limit of monomers in emulsions is around 10 ppm.

**SOLVENTS, COALESCING, AND PLASTIZIZERS:** Nearly all latex polymers paint formulations with a minimum film formation temperature (MFT) of 5°C must contain a low volatility solvent to act as a temporary plasticizer to enhance polymer particle consolidation in film formation. These solvents may or may not be water solu-
from solvent, plasticizers, and other additives to the determination of the polymer composition. For this method to work, the polymer must be unzipped by fast heating to temperatures greater than 400°C in an inert atmosphere. This procedure reduces the high molecular weight polymer to fragments amenable to GC analysis. Normally, the low molecular weight fragments are characteristic of the starting polymer. For example, acrylics generate large amounts of the original monomers. Typically, wet or dry samples can be analyzed either by ribbon or coil probes. The material is pyrolyzed instantly at 700–800°C for 10–20 sec. Normal pyrolysis runs are between 30–40 min. However, with high-speed GC systems, analysis time can be as short as 60–120 sec. Short analysis times are achieved with short narrow columns or high flow rates, high temperature oven ramps, and high speed detectors for high-speed separations.

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**Representative GC Application Areas**

**RESIDUAL MONOMERS**: The residual monomer level in commercial lattes typically does not exceed 0.2% and in many cases is below 100 ppm. Headspace GC or straight GC is an excellent method for determining the types and levels of residual monomers. In a typical GC analysis, between 5–10% of an emulsion is prepared and centrifuged to extract the residual monomers and the supernatant is injected into the GC. The detection limit of monomers in emulsions is around 10 ppm.

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ble, e.g., diethylene glycol butyl ether is water-soluble while Texanol (3-hydroxy-2,2,4-trimethylpentyl isobutyrate) ester alcohol is not. In a typical analysis, about 2% THF/paint mix is centrifuged into insoluble polymer and pigments. The supernatant is then injected into the GC for analysis.

Alternatively, a known amount of the paint or emulsion is put in a headspace vial, sealed and heated to 130°C for 5–10 min and the gas is injected into the GC/MS for analysis.

ASTM methods for the analysis of paints using gas chromatography include: D1943 and D2800 for fatty acids, D2245 for the identification of oils and oil acids, D3960 for VOCs in paints, D3009 for spirits, and D3272 for solvents.

COATING FAILURES: GC, pyrolysis-GC/MS, and headspace GC can be used effectively to solve coating failure problems. For example, if coating failure is due to the use of a wrong (different) batch of paint, one can look at the solvent composition by GC or, by headspace GC, one can look at the solvent composition by GC or, in cases where only the dry paint is available, by headspace GC. By comparing fingerprint data of the residual solvent of the failed paint to the control, one can easily identify whether a sample has been adulterated.

It can be concluded from Figures 11 and 12 that the coating failure is most likely due to the presence of contamination, which has been identified as long-chain hydrocarbons and dodecane.

LOW-LEVEL ADDITIVES AND ADDITIVES: Pyrolysis-GC is also suitable for analyzing low-level additives, which are less volatile due to their relatively high boiling points, for example, waxes and oils. Figure 13 shows a pyrogram of a sample. Each containing low levels of a high boiling point hydrocarbon ranging from about C_{25} to C_{32}. wax/oil. A selective m/e = 57 extraction reveals an ion fragmentation pattern which is consistent with wax/oil components, such as dodecane and tetradecane (Figures 14 and 15).

Other Areas of Application

Additional applications include analysis of condensation polymer systems, alkyl and polyester resins, silicone polymers, polyurethanes, epoxy resins, polyisocyanates, polyamides, vinyl polymers, phenol formaldehyde resins, resin derivatives, and cellulose derivatives.

CONCLUSION

This article has shown that gas chromatography (GC)-based techniques continue to provide vital information to coating scientists and are standard analytical tools for the analysis of coatings and related materials. Many volatiles and semi-volatile compounds such as residual monomers, solvents, plasticizers, and low molecular weight additives such as midewaxes and antifoaming agents can be easily analyzed by GC. For higher molecular weight components, pyrolysis-GC/MS and related methods are applied. New technological advances in the area of high-speed GC/MS and multidimensional GC systems and methods will probably become standard tools in coating analysis in the near future. This is because such systems are now becoming more user friendly, requiring less software and more affordable than in the years past.

GLASSARY

Cold injection: An injection that occurs at temperatures lower than the final oven temperature, usually at or below the solvent boiling point.

Column efficiency: The ability of a column to produce sharp, well-defined peaks. Height equivalent to one theoretical plate, H. The distance along the column occupied by one theoretical plate. N: Number of theoretical plates. N = H/L.

Resolution (R): The quality of separation of two peaks. For two closely eluted peaks, R = (l_{1} - l_{2})/(2w_{1/2}), where l_{1} and l_{2} refer to the first and second peaks from N. l_{1} and l_{2} are the retention times of the second peak. It incorporates both efficiency and separation. Sensitivity: Signal output per unit concentration or per unit mass of analyte. Split Ratio: Split flow rate/column flow rate.

Minimum detectability: D = 2N/S, where N = noise level and S = sensitivity.

References


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March 2005
JCT CoatingsTech

March 2005
FSCT Virtual Learning Conferences

March 17, 2005
UV Curable Coatings I: Coatings for Plastics
Presented by Aaron Lockhart, Bayer MaterialsScience

March 31, 2005
UV Curable Coatings II: Coatings for Wood
Presented by Ron Schweinberg, JHG

April 17, 2005
Advances In Waterborne Resin Technology
Presented by Frederic H. Webber, Air Products and Chemicals, Inc.

May 5, 2005
Corrosion & Coatings I
Presented by Gordon Beveridge, North Carolina State University

May 9, 2005
Corrosion & Coatings II
Presented by Gordon Beveridge, North Dakota State University

Check FSCT's website for additional programs.
Figure 14—Mass spectral data in Figure 13 is consistent with n-docosane.

![Mass Spectral Data](image)

Figure 15—Mass spectral data in Figure 13 is consistent with tetradecane.

![Mass Spectral Data](image)

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Additional applications include analysis of condensation polymer systems, alkyd and polyester resins, silicones, polyurethanes, epoxy resins, polylactones, polylactide, vinyl polymers, phenol formaldehyde resins, resin derivatives, and cellulosic derivatives.

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