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Use of TG/FT-IR in material characterization

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Abstract The use of thermogravimetry (TG) in series with Fourier transform infrared (FT-IR) spectroscopy enhances some of the capabilities of both analytical techniques. TG continues to be an useful method for understanding how the mass of a sample changes as a function of time and temperature, but TG cannot tell us exactly what is happening during transitions. FT-IR is useful for understanding the qualitative nature of molecules and mixtures. However, FT-IR often cannot tell us what happened during a thermal transition if all we can do is examine the sample before and after it is heated. By combining the two methods, an FT-IR spectrometer can monitor the effluent of a TG and allow us to analyze the evolved gas. TG/FT-IR can be used to monitor many types of thermal experiments including cure profiles, solder reflow profiles, and material decomposition. In simple experiments, it can be used to discern subtle differences between what should be identical materials. A summary of recent analyses will be presented.

Keywords TG · FT-IR · Evolved gas analysis · Hot stage microscopy · Jen Chiu

Introduction

TG is a relatively straightforward and basic technique. It uses a balance and a furnace to study the effects of temperature on the mass of a sample. TG determination of decomposition temperature is a valuable screening technique for unknown samples as prior knowledge of decomposition temperature can avoid damage to other thermoanalytical equipment.

TG can tell us many things about a sample. It can tell us where a sample loses water, or some entrained solvent, or volatile component. It can tell us if there is a chemical reaction, such as a degradation occurring while a sample is being heated. However, many of the details of what material is evolving from a sample must be taken on faith based on what we know about the sample, or what we can find in the literature, or we can attempt to analyze the effluent from the TG in an effort to understand what materials are being evolved and when.

FT-IR spectroscopy is another relatively simple analytical tool. A broad band infrared source interacts with a sample and from the pattern of absorption bands that we observe we can deduce molecular structure information. FT-IR works best for single compounds, where you can, with some confidence, assign most, if not all, of the observed absorption bands to a vibrational mode associated with some part of the molecule under evaluation. With mixtures, things get more complicated as it is not always clear which vibration goes with which part of which molecule. This is a challenging task that can usually be accomplished through the use of spectral subtraction or other interpretive techniques. Comparing infrared spectra of a sample taken before and after it is heated will not always allow us to deduce what happened while the sample was heated.

The addition of a few ancillary components can successfully allow the interfacing of these two tools. A heated transfer line between the two instruments and a heated gas cell in the infrared spectrometer allow the safe passage of

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the effluent from the TG through the FT-IR. The addition of software in the FT-IR that allows the collection of a series of sequential infrared spectra completes the basic package. A TG/FT-IR experiment is really two separate experiments that are executed simultaneously. In preparation for these experiments, the FT-IR collects background scans and the TGA collects tare information. After the sample is loaded and the experiments start, the TGA runs through its program of time and temperature and the FT-IR collects a spectrum every few seconds or so until the end of the experiments. After the experiments are complete, we are left with two sets of data. One tells us time, temperature, and sample mass. These are typically curves of mass percent versus time and temperature versus time. A curve of the derivative of mass percent with respect to time versus time is also often added (Fig. 1). The other data set gives us a series of infrared spectra that were collected as a function of time. The infrared spectra are typically accompanied by a Gram-Schmidt reconstruction (GSR), in which each data point basically represents the integrated infrared signal from an individual infrared spectrum (Fig. 2). The GSR often closely resembles the derivative mass percent curve from the TGA. The observable differences between the intensity of the GSR and the derivative mass percent curve are due to different absorptivities of the molecules being evolved. The combination of these two data sets allows us to discover how the infrared spectra change over the course of the TG experiment.

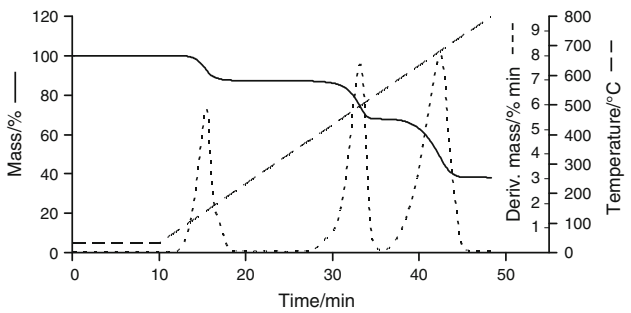

Fig. 1 TG curves for dehydration/decomposition of calcium oxalate monohydrate

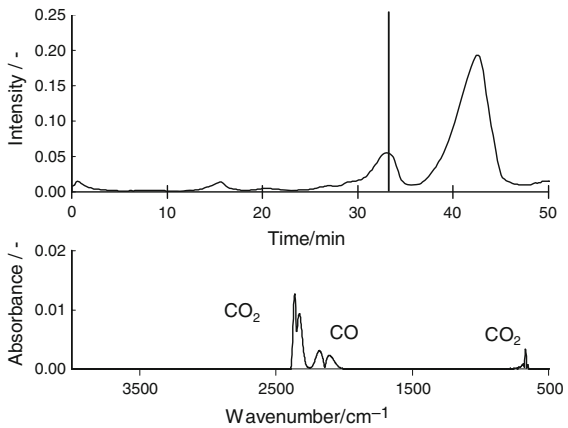

Fig. 2 Example FT-IR curves for dehydration/decomposition of calcium oxalate monohydrate (*top curve* is the Gram-Schmidt reconstruction, *bottom curve* is the spectrum at the peak of the second outgassing event)

Experimental

The experiments discussed here were carried out primarily with a TA Instruments Q5000IR TGA and a Thermo Nicolet 6700 FT-IR spectrometer. Thermomechanical analysis experiments were carried out with a TA instruments 2940 TMA. Hot stage microscopy was carried out with a Linkam THMS600 hot stage.

Discussion

The combination of TG and FT-IR can be used to study many different types of processes or reactions. Listed here are a few general types. The experiments can be used to understand the onset of decomposition and the gases evolved as a sample is heated to higher and higher temperatures. TG/FT-IR can be used to attempt to understand differences between samples that should be similar. Curing reactions, in which samples are often subjected to multistep thermal programs, can be studied by TG/FT-IR to understand how much and which gases are being evolved. Another interesting experiment is the study of solder and flux as they are heated in a simulated reflow profile. Below are some examples of these types of analyses.

Monitoring decomposition reactions

One simple experiment that is often used to promote the utility of evolved gas analyses (EGA), including TG/FT-IR, is the decomposition of calcium oxalate monohydrate by heating to 800 °C in nitrogen. Evaluation of the curve from the experiment suggests the traditional description of this reaction with an initial dehydration of the sample followed by the first decomposition of the oxalate to the carbonate with the loss of carbon monoxide and finally the decomposition of the carbonate to the oxide with the loss of carbon dioxide (Eqs. 1, 2a, and 3 and Fig. 1) [1]. Evaluation of the associated FT-IR data (or mass spectrometry (MS) data, in the case of TG/MS) suggests that this is not exactly the case [2]. During the first decomposition, the spectra produced show the presence of carbon monoxide and carbon dioxide. Clearly something else is occurring during the reaction (Fig. 2). This is typically referred to as a disproportionation reaction in which the carbon monoxide reacts to form carbon

dioxide gas, which is observed by FT-IR or MS, and residual solid carbon, which is observed as a gray tint to the theoretically white final product (Eq. 2b).

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \uparrow \quad (1)$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \uparrow \quad (2a)$$

$$2CO \rightarrow CO_2 \uparrow + C \quad (2b)$$

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \quad (3)$$

In missiles, there is often the case where one or more organic materials, which are situated near critical optical components, are subjected to aerothermal heating and may outgas and affect the neighboring optical system, which may operate in the infrared region. In such cases, it is advantageous to know what materials may outgas and at what temperature. This information can be used to insure that the appropriate material is being used for a particular application. In one example, TG/FT-IR was used to study the gases evolved as an adhesive material was heated ballistically in air to a series of elevated temperatures (Fig. 3). In these experiments, ballistic heating was the equivalent of between 600 and 1100 °C min^{-1}. Evaluation of the infrared spectral data associated with the experiments showed significant degradation, including evolution of ammonia at temperatures above 275 °C (Fig. 4). In this case, the adhesive was recommended for use at in-flight temperatures up to 250 °C; caution was recommended at temperatures around 275 °C; and the material was not to be used if projected in-flight temperatures were to exceed 300 °C.

A similar situation was observed with O-rings that were to be subjected to aerothermal heating. Samples of the O-rings were heated at several temperatures between 120 and 600 °C in air. Rather than looking solely for the onset of significant degradation, the spectra from the TG/FT-IR experiments were used to estimate the potential spectral contamination that might occur within an optical seeker. An example TG data set for an O-ring heated to 600 °C is shown in Fig. 5. An infrared spectrum from the experiment and its constituent components is shown in Fig. 6.

Delamination of laminate materials can occur because of decomposition within the laminate structure and TG/FT-IR can be used to discern the cause of the delamination. Delamination was observed in a laminate radome after

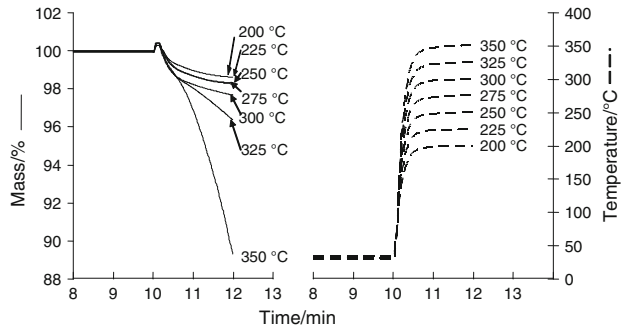

Fig. 3 TG curves of mass percent versus time (*left*) and temperature versus time (*right*) for the analysis of an adhesive at temperatures from 200 to 350 °C

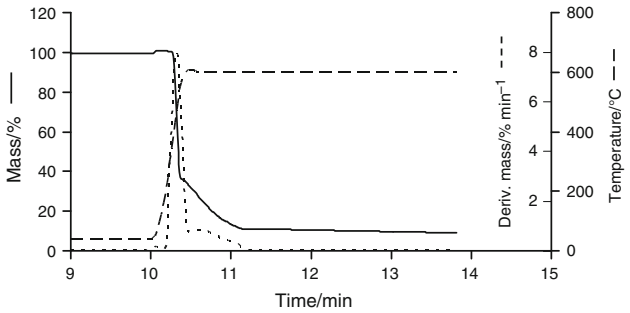

Fig. 5 A portion of the TG curves for O-ring heated ballistically in air to 600 °C

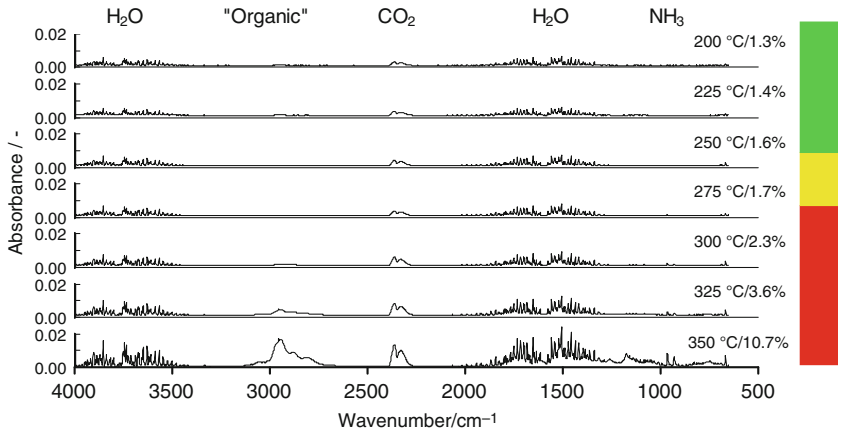

Fig. 4 Graphic depicting, from left, infrared spectra from the TG/FT-IR experiment, experimental temperature, TG mass loss, and stop light graphic, which illustrates recommended temperature ranges

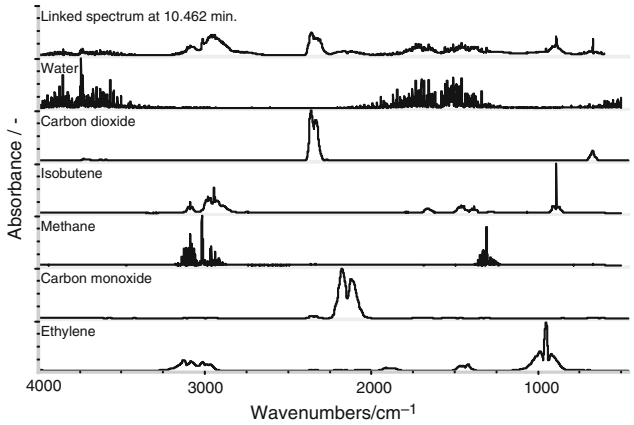

Fig. 6 Infrared spectrum from first peak of TG mass loss in Fig. 5 (*top*) and library spectra of constituent components

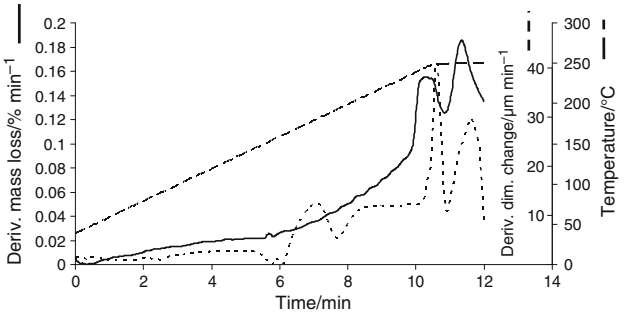

Fig. 7 Overlaid curves from analyses of laminate sample including derivative mass percent versus time, from TG experiment; derivative dimension change versus time, from TMA experiment; and temperature plotted versus time

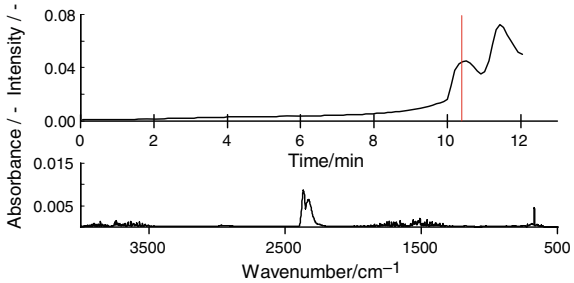

Fig. 8 GSR plot from analysis of laminate sample (*top*) and infrared spectrum from first peak observed in GSR (*bottom*)

activation of a deicing circuit, which was buried within the laminate. TG/FT-IR was used to understand what materials were evolved as the laminate material was heated. Thermomechanical analysis (TMA) was also used to monitor the onset of the delamination event. Figure 7 shows an overlay of a TG and TMA curves as a laminate sample was heated to 250 °C in nitrogen. Both curves show a rapid event at approximately 250 °C. The TMA curve indicates a delamination event and the TG curve indicates a rapid evolution of gas. Figure 8 shows the GSR plot from this

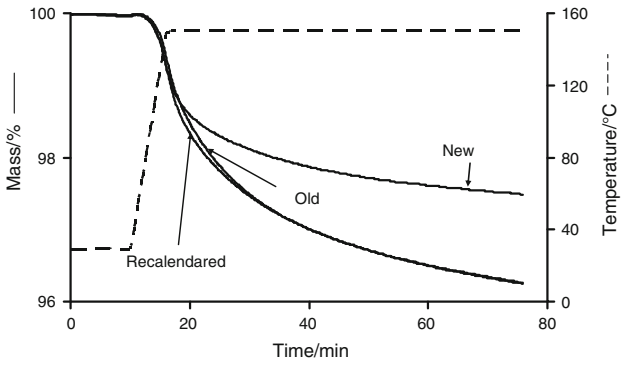

Fig. 9 TG curves for three rubber samples

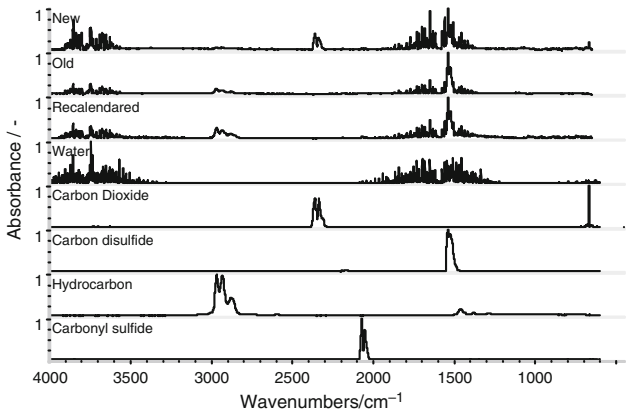

Fig. 10 Infrared spectra from three rubber samples (*top*) and library spectra of observed components

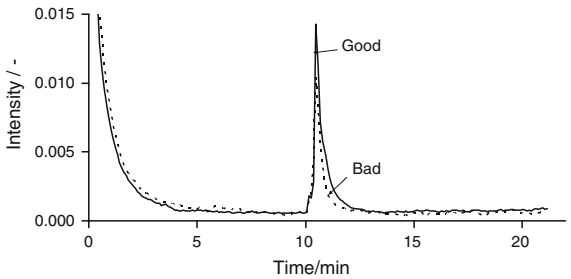

Fig. 11 GSR curves from two ceramic samples

experiment and the infrared spectrum corresponding to this event. Rapid evolution of carbon dioxide and water vapor is indicative of a decomposition event.

Comparing similar materials

TG/FT-IR can be used to compare materials that should be similar. In one such instance, three samples of uncured rubber were received for analysis. One sample was old and out of shelf life. Another sample was of similar age, but had been recalendared. The final sample was a new

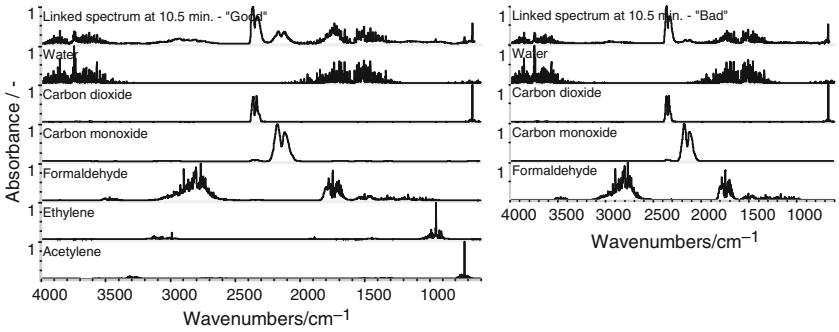

Fig. 12 Spectra of "good" versus "bad" ceramic samples (*top*) and component spectra showing additional components in "good" spectrum

Fig. 13 Transition of a rectangular section of photo resist to a curved section of photoresist to a curved metal structures

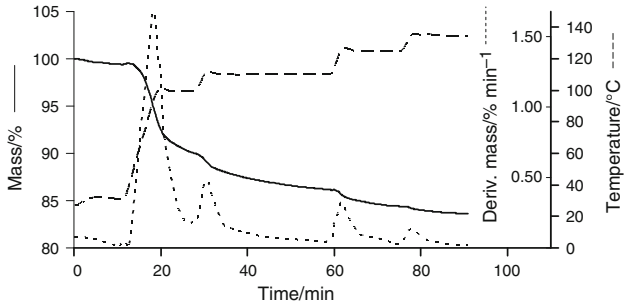

Fig. 14 TG curves for solder resist heated through a four step profile

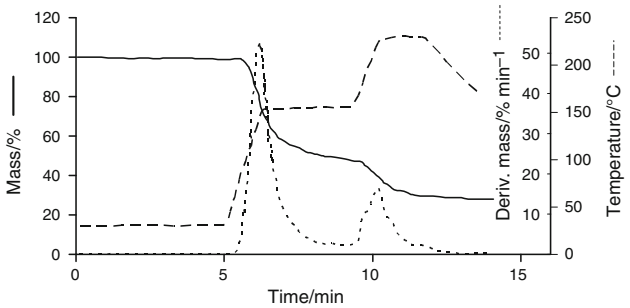

Fig. 16 TG curve of solder and flux during a simulated reflow profile

formulation of the rubber. The three samples were compared by TG/FT-IR and showed some differences. The new sample showed less mass loss than the two older samples while being heated to 150 °C in nitrogen (Fig. 9). Investigation of the associated infrared spectra showed differences in the compounds identified in the evolved gases (Fig. 10). Rheological testing of the rubber samples showed similar trends between the samples.

Another material comparison project involved two samples of a ceramic material. One sample was observed to be more fragile than the other and discolored when heated to 600 °C. When tested by TG/FT-IR, the two materials showed only subtle differences in mass loss and GSR when ballistically heated to 600 °C in nitrogen (Fig. 11). The gases evolved from both samples included water, carbon dioxide, carbon monoxide, and formaldehyde. The sample that did not discolor upon heating also exhibited the evolution of acetylene and ethylene (Fig. 12).

Monitoring cure reactions

The evolved gases from cure reactions can be monitored by TG/FT-IR. One interesting example involved the curing of a photo resist that was used to create unique, curved

Fig. 15 Photomicrographs of photoresist sample from beginning (*left*) and end (*right*) of hot stage microscopy experiment using same thermal profile as TG/FT-IR experiment

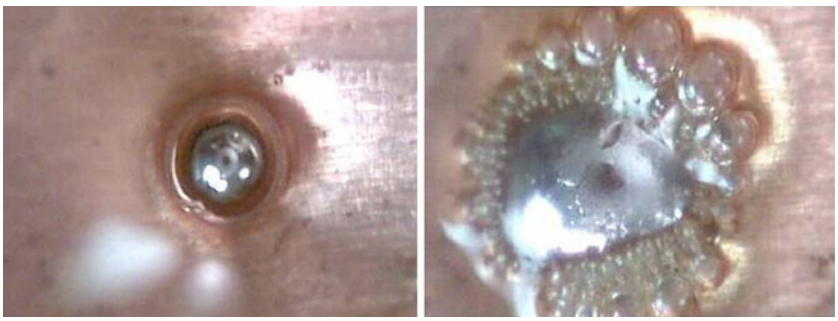

Fig. 17 Photomicrographs from hot stage microscopy experiment of solder and flux before (*left*) and after simulated reflow profile

features (e.g., compliant metal connectors on the surface of a silicon die) [3]. The "as prepared" photoresist is rectangular in cross section. During a partial cure cycle, the resist collapses under the surface tension of the flowing material and forms a curved shape which can be used as a template for advanced shapes (e.g., curved metal contacts for compliant interconnects) (Fig. 13). TG/FT-IR was used to follow the cure in which only residual solvent was found in the evolved gases (Fig. 14). Hot stage microscopy was also used to follow the shape change as a function of the cure profile (Fig. 15).

Monitoring solder reflow reactions

Solder joints are typically formed with the aid of a fluxing agent that cleans the metal surfaces in preparation for the formation of a solder joint. TG/FT-IR can be used to monitor any gas evolved during a reflow profile in an effort to understand the soldering process (Fig. 16). A single solder sphere can be placed in a small copper pan with a sample of flux and be subjected to a simulated reflow profile in the TGA. Hot stage microscopy can be used to monitor the reaction as a function of temperature (Fig. 17).

Conclusions

TG/FT-IR is a combination of two analytical techniques that typically produce results that represent more than either individual technique can. The technique allows analysis of many types of samples. The combined data set can be compared to other analytical tests that are performed under similar thermal profiles.

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