

Thermogravimetric- Infrared Analysis

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Plasticizer Characterization by TG-IR

Introduction

Plasticizers are additives that are added to polymeric material to increase flexibility. For example, phthalates are usually added to hard PVC plastics to make it soft. Many properties of the polymer will be changed by the addition of a plasticizer, such as the glass transition temperature (T_g) which will be reduced dramatically; the hardness which will be reduced; the strength which will decrease and the processability which will be improved. Since

plasticizer is often made up of small molecules, it will migrate to the surface and evaporate from the polymer matrix over time or upon heating. One common example is the smell of a new car which is caused by the plasticizer evaporating from the car's interior polymer parts. Because the plasticizer may be toxic and be harmful to human health, restrictions often apply to some types of phthalates such as in children's toys in the United States and European Union. It may be important to know the plasticizer added to the polymer product and its content.

Thermogravimetric analysis (TGA) is a common technique that is used to study the weight loss during heating. It can tell you the percentage of weight loss quantitatively and accurately. But TGA alone will not tell you anything about the chemical components of the evolved off gas. The hyphenation between TGA and FT-IR is able to identify the off gas from TGA and give a more complete picture of material characterization.

In this note, the sample is a complex mixture of solvent, plasticizer and polymers from a paint and varnish producer who require data concerning the plasticizer and its percentage.

Instrument

A PerkinElmer TGA 8000 and Frontier FT-IR system connected by the state-of-the-art TL 8000 transfer line was used for this analysis (Figure 1)



Figure 1. The TL 8000 transfer line couples a Frontier FT-IR to a TGA 8000.

The advantages of this system include:

- Insulated heated transfer line with replaceable SilcoSteel® liner.
- Heated zero-gravity-effect 'ZGCell' gas cell for the Spectrum instrument incorporating automatic accessory identification, low volume, and efficient sample area purging.
- Control unit incorporating a mass flow controller, particle filters, flow smoothing system, independent transfer line and gas cell temperature controllers, and vacuum pump with exhaust line.
- Automatic triggering of IR data collection from the Pyris software.
- Spectrum Timebase software for time resolved experiments.

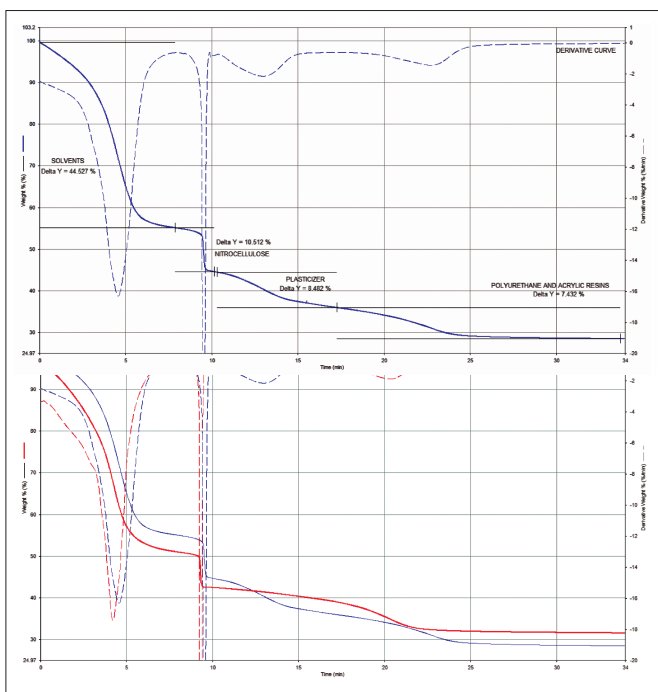


Figure 2. TGA and its derivative curve. Red curve: sample without plasticizer; Blue curve: sample with about 8% plasticizer.

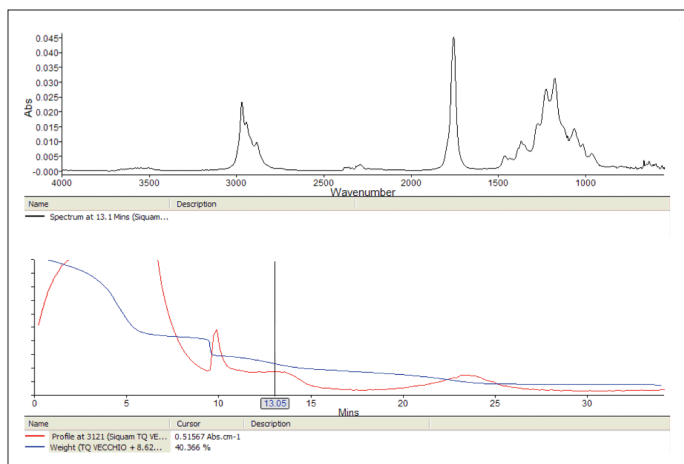


Figure 3. The IR spectrum at 13 minutes.

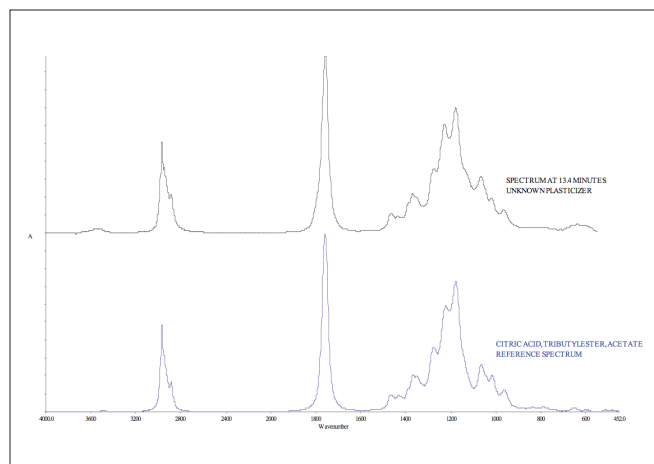


Figure 4. Unknown plasticizer spectrum vs. reference spectrum.

Result

Two samples were analyzed by TG-IR. The red TGA curve is the sample without plasticizer; the blue TGA curve is the same sample with the addition of approximately 8% of plasticizer in Figure 2. The derivative of weight loss is also shown in order to help identify the weight loss event.

For the red curve, the first loss of weight is due to the solvents; the second loss is attributed to nitrocellulose polymer and the third loss is due to polyurethane + polyacrylate polymers. For the blue curve, the first loss is from solvents; the second loss is again from nitrocellulose polymer; the third loss is supposed to be from the added plasticizer and the fourth loss is from polyurethane + polyacrylate polymers. All components were identified from gaseous fragments in TG-IR. So by comparing the red curve with the blue curve, it can be seen that the only difference is the weight loss due to plasticizer from the blue curve. The content of plasticizer is determined to be 8.48%.

In order to identify the plasticizer, the IR spectrum is used in Figure 3. The IR spectrum at 13 minutes is used because from TGA curve it can be seen that the evolved gas at this point is from the plasticizer. By looking at this IR spectrum and comparing it to reference spectrum (Figure 4), it can be shown that the plasticizer used here is citric acid, tributylester, acetate.

Conclusion

The TG-IR hyphenation technique has been widely used for the polymer industry, in this case the identification of plasticizer in paint. It combines the strength of TGA and FT-IR analysis and offers a more comprehensive material characterization. The PerkinElmer TG-IR system with the TL 8000 transfer line has proven to be the ideal solution for this analysis. It is easy to use and its design features guarantee the highest quality and most reliable results.