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Nota de aplicación

RADIAN ASAP for Simple Mass Spectral Screening of Polymer Formulations

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This is an Application Brief and does not contain a detailed Experimental section.

Abstract

The analysis and monitoring of additive chemical profiles plays an important role in advanced polymer formulation manufacturing research and development. The RADIAN ASAP System was used for the rapid analysis of a polymer formulation, with minimal sample preparation and the deployment of a thermal gradient to help deconvolute the complex sample. Both the polymeric material itself and the processing additives were easily identified using this approach. The quick and simple technique could be deployed by analytical scientists or formulation engineers to easily observe the components of their advanced materials and speed up the decision-making process in formulation design.

Benefits

- Limited sample preparation required
- Temperature ramping functionality enables thermal deconvolution of complex samples
- Complementary data to traditional polymer property measurement techniques such as thermal analysis and rheology
- Provides access to mass based chemical identification without recourse to central analysis labs or through time consuming gas or liquid chromatographic – MS techniques
- APCI-based ionization provides information on intact analytes removing requirement for NIST spectral database comparison
- Data available within minutes to enable accelerated business decisions

Introduction

In the development and manufacture of advanced polymer formulations, materials scientists, chemists, and engineers take multiple complementary data streams from a wide variety of measurement techniques and synthesize these data into information providing deep insight into their products. Chemical and physical property analyses such as TGA, DSC, Rheology, GC- or LC-MS and spectroscopic methods are of crucial importance. They are implemented for traditional QA/QC, but also for innovation in formulation research and development and for optimization of the production workflow. Unfortunately, in most cases the lead time in data generation is several hours or even days. This includes the sample preparation, the measurement runs

and treatment of raw data, analysis and reporting. Compressing this process to the scale of minutes in total, would help to support strategic decisions and close the gap between information and impact.

In this work, we illustrate the benefits of using fast, direct analysis with mass detection to discover and monitor polymer formulation additives as a complementary technique to traditional materials property measurement techniques such as thermal analysis or rheological profiling.

Results and Discussion

A polymer formulation made up of PEG 600 and four polymer processing additives were analyzed in triplicate using the RADIAN ASAP system. The formulation was dissolved in 9:1 toluene:methanol with 0.1% formic acid to make a solution of 1 mg/mL. Prior to analysis, 1 mL of the solution was pipetted into an ACQUITY vial to produce a solution that occupies a known volume and depth.

A new glass sampling rod (capillary) was used for each analysis. Using the RADIAN ASAP system, each glass capillary was cleaned using a rapid, automated “bake out” procedure that exposes the tip of the capillary to a stream of high-temperature gas to burn off any residual contamination transferred from the packaging of the glass capillary. A simple “dip and swirl” technique was used to sample the solution for 15 seconds for each analysis. Pipetting 1 mL into the ACQUITY vial, and sampling for identical amounts of time, ensured that the exposure of the glass capillary to the analyte was reproducible throughout the experiment.

When dealing with highly complex samples, a degree of separation is beneficial. RADIAN ASAP offers features such as the ability to apply a temperature ramp, or thermal gradient, which separates components based on their different boiling points. Figure 1 shows the stepwise temperature gradient method as built in MassLynx control software along with the total ion chromatogram (TIC) of the analysed formulation overlaid with the observed temperature gradient. The chromatogram is a trace of all the ionised species detected by the system over the course of the 6 minute temperature gradient.

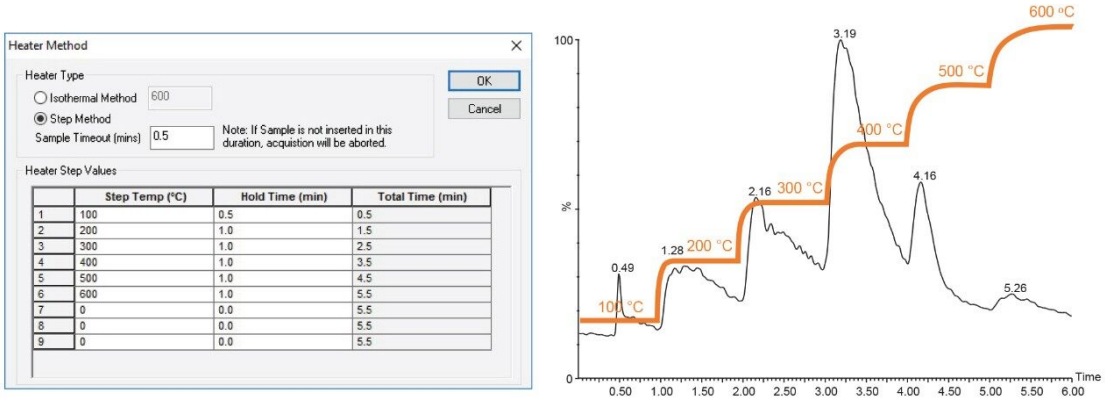

Figure 1. Stepwise Temperature Gradient Method in MassLynx Software and the resultant TIC overlaid with the observed temperature profile.

Figure 2 again shows the resulting thermal profile TIC from the pre-programmed temperature ramp and offers a view of the recorded spectra evolved at different temperatures along the temperature ramp experiment. Key components appear as each boiling point is reached in the thermal gradient. Typically, smaller, lower mass species appear at lower temperatures and larger, heavier mass species appear at higher temperatures. This allows a degree of separation and deconvolution of complex samples.

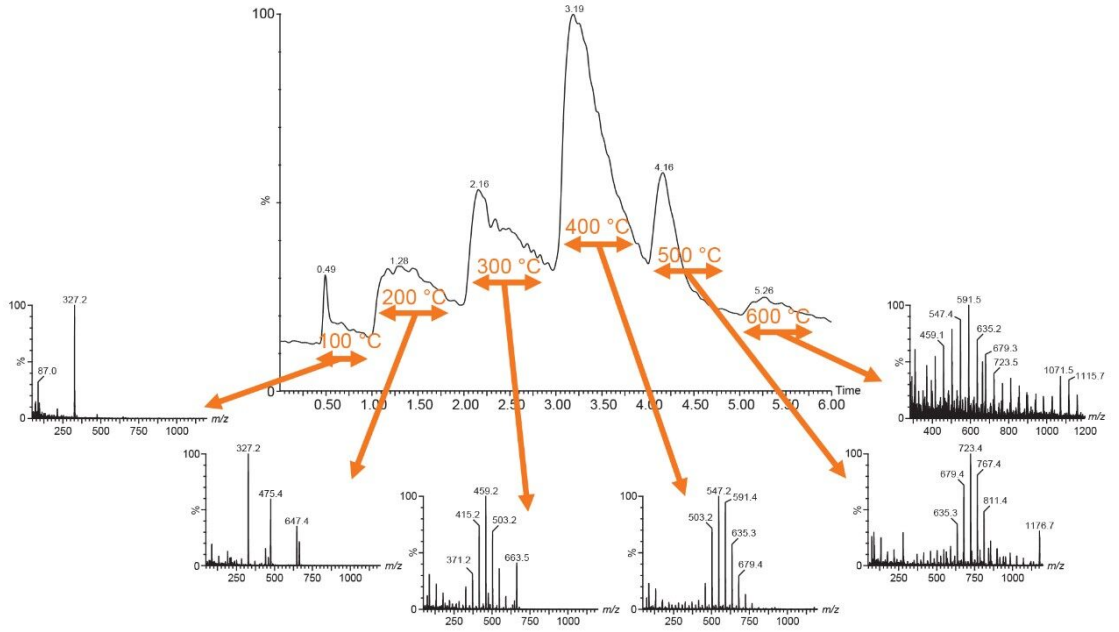

Figure 2. TIC from analysis of the polymer formulation showing spectra evolved at different temperatures along the temperature ramp experiment.

Figure 3 assigns each spectra with the structures of the additives or names of species detected at each stage of the thermal ramp. In this example, the important polymer additives are detected at lower temperatures, except the higher mass additive Irganox 1010 that is observed at 500 °C. The polymer itself appears at higher temperatures – starting at 300 °C all the way up to 600 °C. The APCI based ionisation technique employed by RADIAN ASAP allows for increased transmission of intact analyte ions compared to electron impact (EI) based ionisation usually found in hyphenated Thermal-MS or GC-MS measurement techniques. The information rich data provided by RADIAN ASAP reduces the need to refer to database comparisons such as NIST spectral databases for identification.

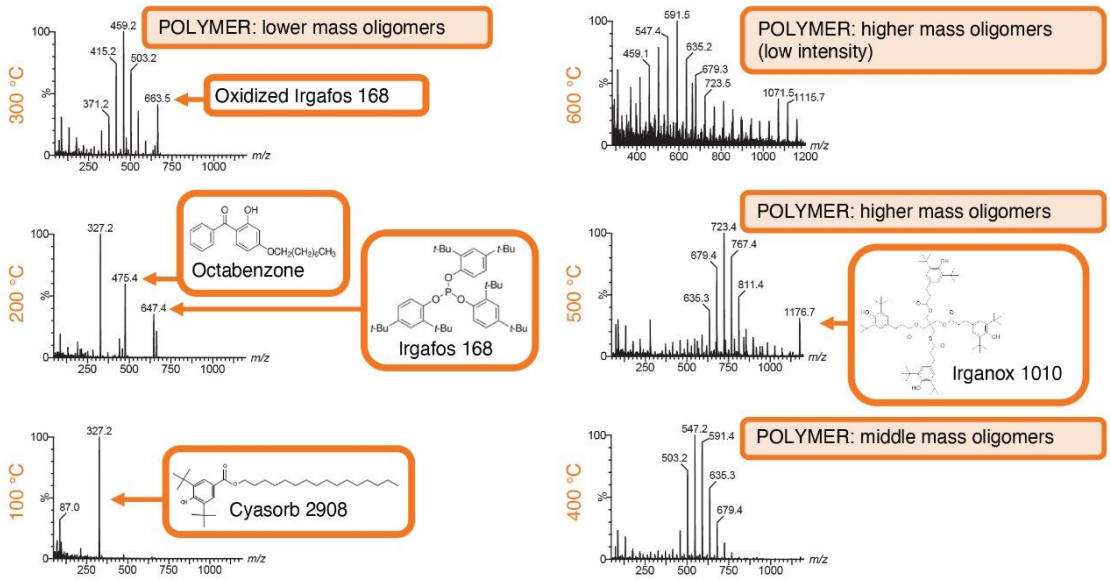

Figure 3. Observed mass spectra detected assigned with the structures of the additives present at each stage of the thermal ramp.

This approach could be used across multiple workflows in the polymer formulation manufacturing industry, including formulation research and development by tracking levels of key formulation ingredients through formulation use cycle; QC batch release based on presence of active ingredients; and competitor analysis by determining chemical points of difference between competitor formulations.

Conclusion

The RADIAN ASAP System offers direct insight into the chemical behavior of polymer formulations. In this case both polymer additives and oligomeric species from the polymer itself were detected using a simple analytical protocol. The data was generated within minutes and can be readily combined with physical property measurements to quickly inform key business decisions.

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