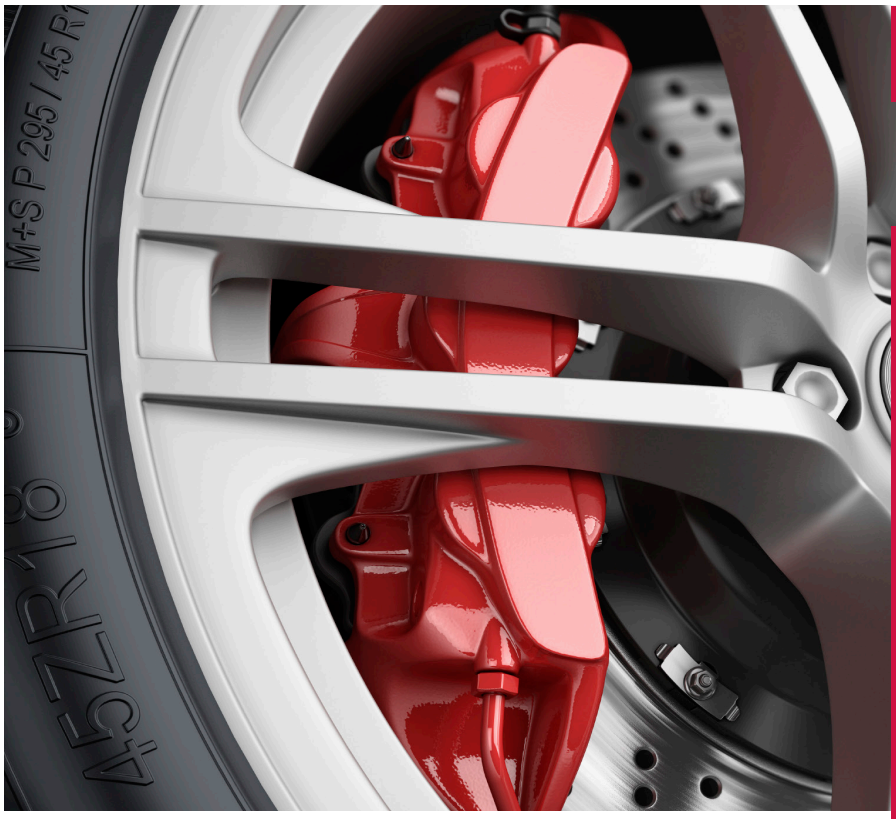

APPLICATION NOTE

Thermal Analysis

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Rubber Analysis with the PerkinElmer TGA 8000

Figure 1. TGA 8000 Thermogravimetric Analyzer.

Introduction

Thermogravimetry has been used for years to quantify the components of automotive rubber products, namely oil, polymer, carbon, and inorganic filler. While this separation is straightforward conceptually, it challenges the performance of Thermogravimetric Analyzers (TGA) in order to achieve reliable accuracy and reproducibility. Since this is also a routine quality test[1], there are the additional challenges of reducing the test time and automating the analysis. Fortunately, the PerkinElmer TGA 8000™ (Figure 1) offers significant improvements in all areas for this analysis.

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For the Better

Method

The test routine consists of loading a weighed sample in a tared pan into the closed environment of the TGA test chamber which is then purged with nitrogen to eliminate oxygen. The sample is then heated to a temperature that will drive off the oils, but not decompose the polymer, where it may be held isothermally until the weight is stable. The sample is then heated to a sufficient temperature to decompose the polymer that is still in the pyrolytic atmosphere of nitrogen. What remains of the sample in the TGA at this point is carbon and inorganic filler, which are next separated by adding oxygen (in air) to the purge stream. Finally, the sample is cooled, weight loss calculations are performed, and the next sample is loaded. An example of this analysis can be seen in Figure 2a and 2b, the separation of the components of an automotive rubber sample.

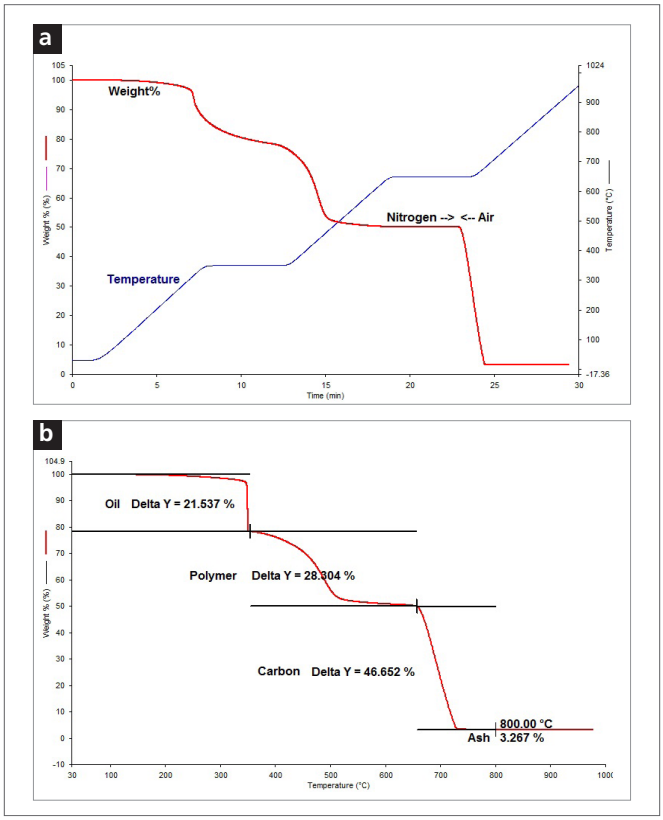

Figure 2a , 2b. The top figure shows weight loss data versus time using a stepwise temperature program. The bottom shows above determination of extender, polymer, carbon, and filler with temperature as the X-axis

TGA 8000 Improvements for Rubber Analysis

Sample Handling

The completely re-engineered and patent-pending TGA 8000 autosampler provides the means for organizing the sample stream and for loading the samples. Designed for reliability and user convenience, this autosampler handles loading and unloading, whether running samples continuously around the clock, or just running the occasional sample. The Pyris Player™ software organizes the methods and tracks the results in a simple, easy-to-read format.

Atmosphere Control

The TGA 8000 offers additional flexibility and the highest performing atmospheric control system on the market. The sample atmosphere is controlled using highly accurate, dual, mass-flow controllers controlling two samples, and one system, purge gas flows. Since the purge rates are under digital control, methods can be set to specify the desired purge types, rates, and switchover points. Moreover, since the purge-rate-versus-time signals are stored with the data files, you can always confirm afterwards what purge flow was in effect, and that there is no chance that a gas cylinder ran out of gas mid-experiment. By programming a rapid nitrogen purge at the beginning of a method, the operator can facilitate purge-out of oxygen prior to pyrolysis. The new Gas Mixing Device (GMD), GMD 8000™ accessory is also available for introducing a three component purge or for programming a continuously changing purge mixture.

Wider Temperature Range, Exceptional Performance

Based on the proven performance of the PerkinElmer microbalance, the TGA 8000 provides exceptional temperature control and baseline stability. The TGA 8000 extends the standard furnace upper temperature to 1200 °C and provides a more robust thermocouple to support higher temperature operation. If a scan needs to be started below lab temperature, or a more rapid cool-down is needed to improve turnaround time, there is a sub-ambient cooling system that can handle it. Improved baseline performance makes achieving 0.1 % accuracy possible without the need to subtract a baseline.

Analysis of Rubber

The goal of the TGA rubber analysis is to come up with values for the oil-extender, polymer, carbon, and inert filler. From the TGA curve, such numbers can be easily determined (Figure 2b). However, the components of rubber are themselves each a mixture of materials having a range of molecular weights and thermal stabilities. As the rubber sample is heated and volatile components are evolving, first the lower molecular weight and less well-bound components are coming off, and then at higher temperatures, the higher molecular weight species are driven off. There is also an overlap region where the polymer is beginning to degrade, while the heaviest of the oil extender components are still evolving. Therefore, depending on the thermal program, the separation may indicate different fractions of extender and polymer. When this is the case, the best approach to characterize the rubber is the use of methods that are optimized for separation, reproducible, and relatively independent of sample size and surface area. Such methods call for slow scan rates or isothermal dwell times in the critical separation regions, and, in order to minimize test time, faster scan rates in the non-critical temperature regions. The TGA 8000 offers innovative features and tools specifically designed to optimize this separation.

Variable Rate Analysis

This new feature enables a method that starts at an initially rapid heating rate, but then decreases as a function of the rate of mass loss. Therefore, without having to define the critical temperature regions, the heat rate automatically slows to allow each process to go to completion. An example of this can be seen on the next page in Figure 3. One advantage of this method, at least in principle, is it applies to all samples and conditions and therefore relieves the operator from having to make specific choices for dwell temperatures and times[2].

Stepwise Analysis

This method steps quickly between the optimum separation temperatures, which result in the most reliable and time-efficient

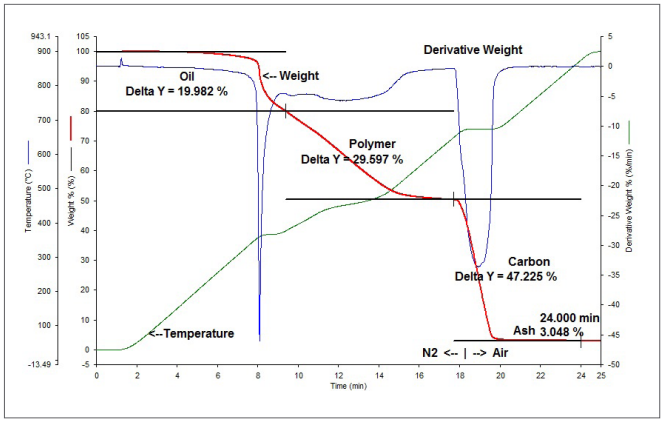

Figure 3. Variable Rate analysis of rubber sample using a 40 °C/min heating rate that slows during weight loss regions

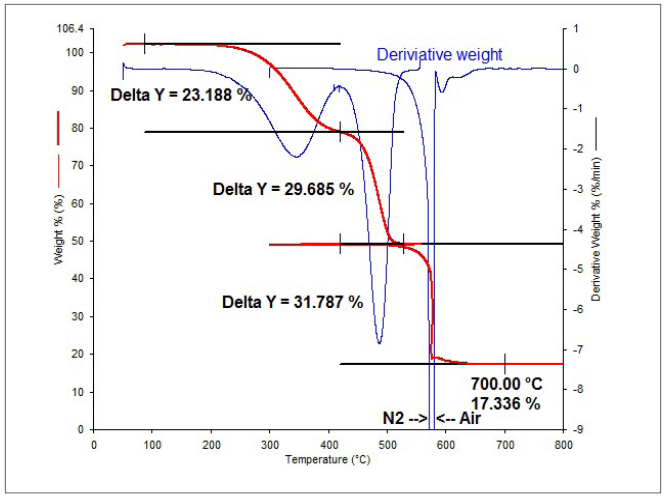

Figure 4. Automotive rubber foam TG analysis using ASTM® D 6370 method.

method of sample analysis, particularly in routine QC of incoming material. Using this approach, the sample can reach an equilibrium mass loss under identical temperature conditions. The TGA 8000 has demonstrated exceptional temperature accuracy over a range of conditions, including when the sample is isothermal[3]. The variable rate analysis is a good starting point for selecting the isothermal separation temperatures for stepwise analysis.

AutoStepwise Analysis

Similar to the variable rate analysis, this technique determines the temperatures for the dwell times by evaluating the real-time weight loss data and triggering a dwell point—or slow scan rate step—based on a criterion for rate of weight loss. The length of the dwell—or slow scan—step depends on a second criterion. After this exit criterion is met, the heating rate returns to the original heating rate until the next dwell onset criterion is met. As a result of being able to control the criteria, the degree of completion of the dwell process on a percent basis can be predetermined, leading to improved precision.

Constant Heating Rate Analysis

This original TGA method has the advantage of historical precedent, and it should give results independent of temperature calibration since weight loss steps can be selected using the derivative weight loss signal to determine the start and end of the weight loss points on the weight curve (Figure 4). In this example, the ASTM method calls for cooling to 300 °C after pyrolyzing the polymer and before oxidizing the carbon. This method takes twice as long as the variable rate methods, but it ensures the completion of the pyrolysis step.

Multiple Mode Analysis

One unique aspect of the Pyris™ software is that one method can contain multiple Variable Rate and AutoStepwise method steps. This means an AutoStepwise™ step can be tailored to optimally characterize the loss of volatiles, so that the exit criterion can ensure uniformity; and then use a Variable Rate step, or steps, with different criteria to optimize higher temperature separation points.

Evolved Gas Analysis

If an evolved gas analyzer (EGA) is attached to the exit port of the TGA it can be used to identify the material coming off the sample. This helps choose dwell temperatures for a stepwise separation, so that the dwell temperature is sufficiently low to exclude the higher temperature weight loss components.

Conclusion

The TGA 8000 offers improvements in performance, capability, and flexibility that provide the tools to develop optimum thermogravimetric separations. The new autosampler facilitates sample handling and provides the structure for tracking and analyzing a continuous stream of TGA test data. To identify the evolved gases from a TGA analysis, PerkinElmer provides interfacing of the TGA 8000 to infrared spectrometers, gas chromatographs, and mass spectrophotometers, all of which are supported by one world-wide service organization.

Reference

1. See ASTM® Methods: E1131-08(2014) and ASTM® D 6370-99(2014),
2. "Use of the TGA8000 for Variable Rate Analysis"
3. "TGA8000 Temperature Performance"

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