PYRIS 1 TGA / TGA 7

TGA Separation of Filled Polyethylene Using AutoStepwise Software

Introduction

New hardware and software capabilities essential for increasing productive operation of thermogravimetry (TGA) in your laboratory are accomplished with several new innovations. Pyris™ Software for Windows® is the core of Perkin-Elmer's thermal analysis family of instruments. It combines the power of the Microsoft® Windows NT® operating system with the flexibility of method development to fully support your laboratory's network environment.

The Pyris 1 TGA, and its optional autosampler accessory, is a system that will not only boost sample throughput, but also improve analytical reproducibility. This is accomplished with the Pyris 1 TGA's thermostat-controlled weighing balance enclosure, the new segmented furnace chamber, and many other engineering innovations.

Couple our advanced hardware with a new and improved advanced software package – TGA AutoStepwise software – and you have a complete TGA system that provides answers to your toughest problems. This application note is an example of what you can expect from Perkin-Elmer.

AutoStepwise TGA Software

Thermogravimetry is used to quantitatively determine the components in a polymer or elastomer formulation by separating the components by their relative thermal stability. In order to resolve materials with similar thermal stability, it is necessary to either heat very slowly or hold isothermally at a temperature that favors one weight loss over the other.[1] In developing an efficient test one needs to balance the needs for resolution, accuracy and test time. The advantages and disadvantages of various separation methods have been previously reviewed.[2]

The Pyris AutoStepwise software offers some unique capabilities for the development of efficient TGA separations with the Pyris 1 TGA as a stand-alone analyzer or with the autosampler accessory. It provides for the use of programmable criteria to automatically determine the start and end point of thermal weight loss events, and also allows for switching between various preprogrammed heating rates or isothermal steps in order to optimize the analysis. In this way, an efficient method that heats the sample rapidly between weight loss regions, and slows down or stops heating during rapid weight loss regions is generated.

Purpose

To develop an efficient and reliable TGA separation method for a polyethylene formulation containing a lubricant, carbon black, and inert filler using the Pyris AutoStepwise software.

Experimental

The material analyzed was a low density (mp 98°C) polyethylene material. The specimen was cut from the middle of a pellet using a razor blade, and it was placed in a platinum pan in a standard TGA furnace. A survey scan was performed at 50°C/min in order to determine the values of the criteria to be used. A second sample was then prepared and run using the parameters listed in Table 1.

Figure 1 shows the thermogravimetric survey scan, including the weight loss curve and first derivative. From this data it is clear that the weight loss events are not completely resolved. The criteria to be used for the AutoStepwise analysis can be determined from the rate of weight loss in the survey scan. From a Delta Y calculation on the derivative curve, it was found that the greatest rate of weight loss for the smallest peak (that of the lubricant) was 0.274 mg/min.

Sample	Polyethylene	
Instrumental	Analyzer	Perkin-Elmer TGA
	Sample weight	5.63 mg
Environmental	Initial purge	30 cc/min nitrogen
	Oxidative purge	30 cc/min air above 800°C
Method Inputs	Temp 1	25°C
	Heating rate	50°C/min
	Temp 2	900°C
	Step On Criterion	0.10 mg/min
	Step Off Criterion	0.01 mg/min
	Step Rate	0.10°C/min
Method Generated	Steps inserted	336.5 – 337.4°C
		408 – 409.7°C
		830.0 – 831.8°C

Table I. TGA AutoStepwise method parameters. These parameters were obtained from data of the survey scan depicted in Figure 1.

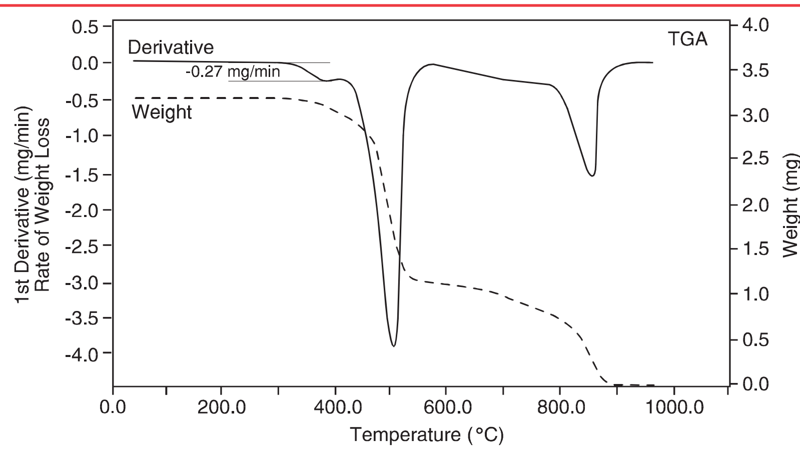

Figure 1. TGA separation of filled polyethylene survey scan at 50°C/min.

Accordingly, a Step On Criterion of 0.100 mg/min was selected for the AutoStepwise scan. Using this method, when a rate of weight loss of 0.100 mg/min is detected, the heating rate is automatically reduced from the initial rate of 50°C/min to that of the Step Rate, which has been selected as 0.1°C/min. The net result is that the AutoStepwise software inserts a slow scan step into the original program whenever the rate of weight loss exceeds the Step On Criterion.

Alternatively, the Step Rate can be selected as isothermal. In this case, the software would insert an iso-thermal step when the Step On Criterion is met. In either case, the slow or isothermal step is terminated, and the original program rate resumed when the Step Off Criterion is met. That is, when the rate of weight loss is less than the Step Off Criterion, the software returns to the original heating rate. In this way, the AutoStepwise software generates a program with rapid heating rates in regions of little weight loss activity and slow heating rates or isothermal dwell times in regions of weight loss.

When using AutoStepwise software, two methods are generated. One method, the one containing the run-time criteria just discussed, is recalled in the Method Editor. The second method, saved with the data, contains the actual stepwise program generated by the AutoStepwise analysis. This stepwise method can be viewed and re-entered, if desired, for subsequent sample analysis. Using this re-entered stepwise method ensures that each sample is analyzed the same way. Moreover, a method can be further optimized by increasing the heating rate between dwell steps and adjusting the dwell temperatures.

Results

The results of the separation can be seen in Figure 2. The Y1 scale is weight percent, Y2 is the rate of weight loss (the time derivative), and the X scale is temperature. The first weight loss is the volatilization of the lubricant, the second is the thermal depolymerization of polyethylene, and the third is the oxidation of carbon black.

The first two events are triggered by the thermal stability of the components. The third step is triggered by the switch of the purge gas from nitrogen to air at 800°C, as programmed into the method. At each of these weight loss events the rate of weight loss exceeded the Step On Criterion, thus causing the

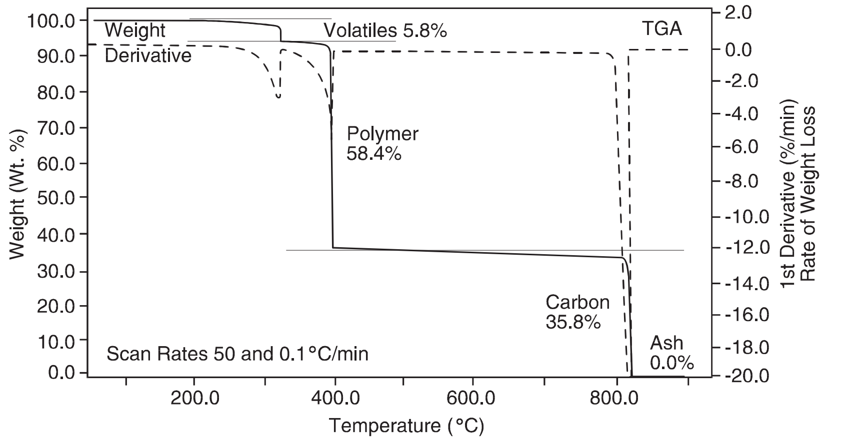

Figure 2. TGA separation of filled polyethylene using AutoStepwise Mode.

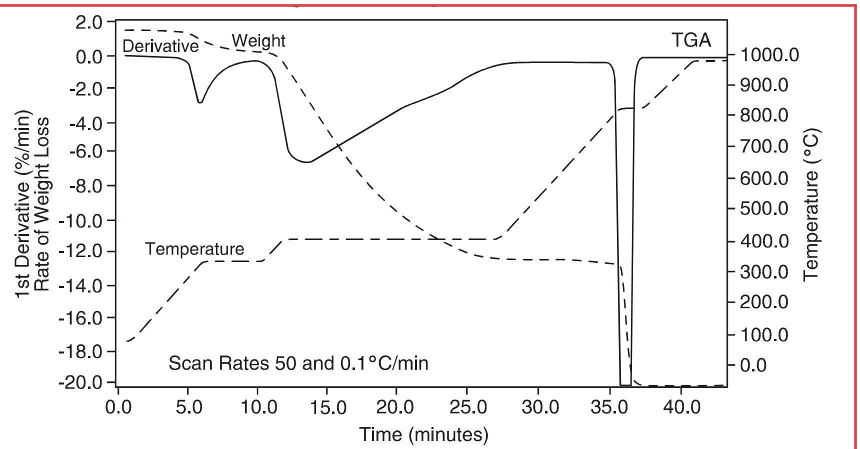

Figure 3. TGA separation of filled polyethylene using AutoStepwise Mode.

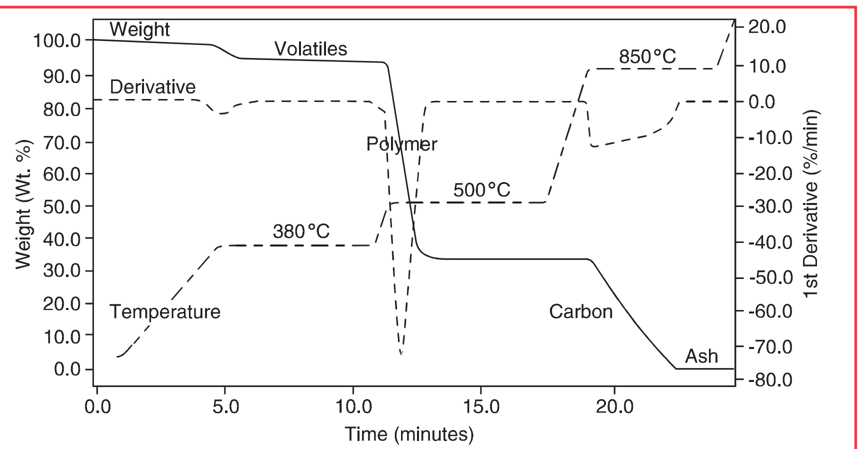

Figure 4. TGA separation of filled polyethylene using an Optimized Stepwise Method.

rate of heating to decrease from 50 to 0.1°C/min until the weight loss event is completed.

The completion of each process can be seen in Figure 3, which shows the rate of weight loss and the sample temperature on a time scale. The calculations for the percent of each component are performed on either plot (Figure 2 or 3) using minima in the derivative curve to assign the demarcation points between thermal events. Figure 4 shows how the method further optimized to reduce the test time to less than 30 minutes.

Conclusion

The Pyris AutoStepwise software was used to expedite the development of an efficient and reliable stepwise analysis method. The percentage of lubricant, polymer, carbon, and inert filler were quantitatively determined. This approach is equally applicable to a wide range of product mixtures, not only of polyethylene as shown here, but also of other thermoplastics, composites, cosmetics, elastomers, and food formulations.

References

1. R.B. Cassel, *Use of the System 4 Microprocessor Controller in the Thermogravimetric Analysis of Polymers, Additives and Fillers*, Perkin-Elmer Thermal Analysis Application Study No. 27, The Perkin-Elmer Corporation, Norwalk, CT (1978).
2. R.B. Cassel, *Stepwise Thermogravimetric Analysis: A Comparison with other Methods, including the Rate-Dependent, Variable Rate Method*, NATAS Paper No. 55 (1991).

Additional Readings:

3. C.M. Earest, Editor, *Compositional Analysis by Thermogravimetry*, ASTM STP997, Philadelphia, PA (1988).
4. E.A. Turi, Editor, *Thermal Characterization* of *Polymeric Materials*, Academic Press (1997).

Ordering Information:

Part Number	Description
N537-0670	TGA AutoStepwise software

PERKIN ELMER

Look to us. And see more.

Visit our Website **at www.perkin-elmer.com.**

The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0010 USA
Tel: (800) 762-4000 or (203) 762-4000 Fax: (203) 762-4228

ISO 9001 CERTIFIED

Order No. D-5994 January 1999 KG019902 Printed in USA. © 1999 The Perkin-Elmer Corporation